MINDO/3 STUDY OF SOME CYCLIC CARBENES

by

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「The fear of the LORD is the beginning of wisdom,

And the knowledge of the Holy One is understanding.」

Proverbs 9:10

(NASB)

CONTENTS

ABSTRACT

PART 1

In the singlet state, cyclopropenylidene(I), Cyclopropylidene(II) and cyclopentadienylidene(III) all have their lone pairs lying on the molecular plane. MINDO/3 calculations indicate that (I) and (II) have a singlet ground state, but it is a triplet ground state for (III). Aromaticity accounts for the greater stability and nucleophility of (I) over the other two carbenes. On the other hand, the emptiness of the p_π orbital of the carbenic centres of (II) and (III) result in their greater electrophilicity, over (I). In the triplet state for (III), delocalization is important; it attributes much for its stability over the singlet state. The triplet and singlet energy separations for (I) and (III) are particularly large. The apex angle of these carbenes increases pronouncedly on transition from singlet to triplet state. The electron correlations are important for the singlet state of (II), (III) and the triplet state of (I). For each system, the electronic structure and its influences on geometry and reactivity are discussed.

PART 2

The concerted non-least-motion insertions of all three carbenes into H_2 proceed with two distinguishable steps, an electrophilic phase followed by a nucleophilic phase. The electrophilic phase is characterized by the formation of a three-centre bond; electron flows from the bonding orbital of H_2 into the "empty" C_1 p_π orbital of the carbene. In the nucleophilic phase, the H-H bond is broken and the carbene lone pair attacks the anti-bonding orbital of H_2.

In the reaction of (I) + H_2, the high population in C_1 p_π orbital of (I) hinders the formation of the C-H_2 three-centre bond, resulting in high activation energy (19 kcal/mol) and late transition state, in comparison with the corresponding reactions of (II) and (III). [The activation energies for (II) + H_2 and (III) + H_2 are about 6 kcal/mol and 2 kcal/mol, respectively]. Due to the presence of the diene system in (III), which serves as a reservoir for electrons, a complicated pattern for the variation of C_1 electron density throughout the reaction is resulted. Hence, the charge on H_2, instead of that on C_1, is used to define the two phases of the reaction (III) + H_2. This reservoir of electrons in (III) promotes rapid population redistribution in the system, causing an abrupt change in energy and geometry of the system in the electrophilic phase of the reaction. Delocalization of π electrons is important for the reaction of (III); this can be deduced from the five of similar length C-C bonds after the aforementional rapid redistribution in the reaction. Besides, the conjugation of the diene with C_1 p_π orbital of (III) stabilizes the system during the reaction of (III) + H_2 and contributes much to the lowering of activation energy.

PART 3

The least-motion prototype insertions of (I), (II) and (III) involve HOMO-LUMO crossing, hence requiring high activation energies. Also, the repulsions between the lone pairs of carbenes and the H_2 σ bond are also reflected in the much higher energy barriers of the least-motion reactions over the corresponding non-least-motion reactions. All these is reflected in the present study of the least-motion H_2 insertions of (I), (II) and (III).

For each of the least-motion reactions, two distinguishable steps, an electrophilic phase and a nucleophilic phase, are observed.

The activation energies for the insertions of (I), (II) and (III) into H_2 are 90, 44 and 37 kcal/mol, respectively. The positions of the transition states are very close to the turning points, with electronic structures similar to those of the reactants. For all three reactions, there are drastic changes in energies, geometries and electronic structures around the saddle points. These changes are much sharper than those in the corresponding non-least-motion reactions. All three reactions are characterized by an abrupt fall of energies (about 120 kcal/mol) in the nucleophilic phases.

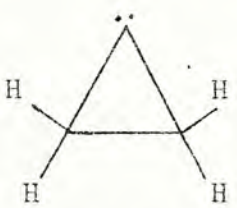
PART 1

ELECTRONIC AND GEOMETRICAL PROPERTIES OF CYCLIC CARBENES

1.1 Introduction

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated acyclic carbenes[1,2]. However, studies on cyclic carbenes are still in infancy. Therefore theoretical studies of these species should be valuable for the understanding of their chemical nature. In this work, MINDO/3 calculations have been carried out on the cyclic carbenes cyclopropropenylidene (I), cyclopropylidene (II) and cyclopentadienylidene (III). The purpose is to investigate their electronic distribution, geometrical properties and relative energies of their different spin states. In Parts 2 and 3, their reactivities toward H_2 will be discussed in detail.

(I)



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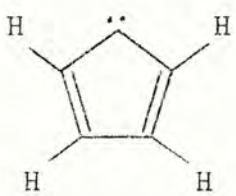


(III)

These three carbenes are cyclic ones with many similar properties, e.g., in singlet state, they all have their lone pairs lying on the molecular plane. But they do differ from one another in many aspects:

(i) There are two π electrons in (I), attaining aromatic stability by the delocalization of the π electrons to the empty p orbital of the

carbenic centre. On the other hand, there is no π electron in (II). In (III), there are four π electrons in the diene system and delocalization does not extend to the carbenic centre. In the triplet state, with one electron in the p_π orbital of the carbenic centre, delocalization of π electrons again becomes important.

(ii) In (I), there is no hyperconjugative interaction, while such interaction is present in (II) and (III).

(iii) An EHMO calculation[3,4] predicts a triplet ground state for (III) and singlet ground states for (I) and (II). However, INDO calculations[5] lead to singlet ground states for all three species.

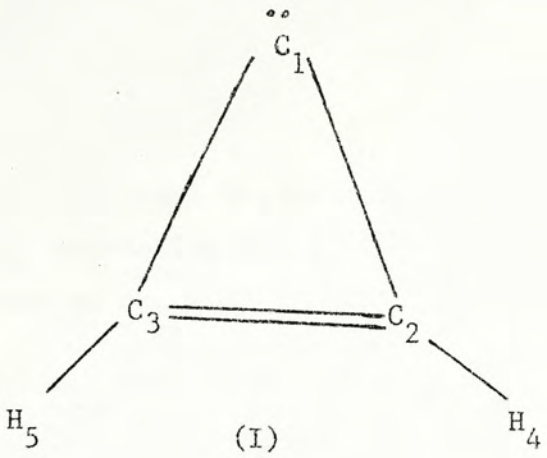
(iv) Due to the smallness of the ring size, considerable strain is present in (I) and (II). But it should not be a factor in (III).

1.2 Method of Calculation and Results

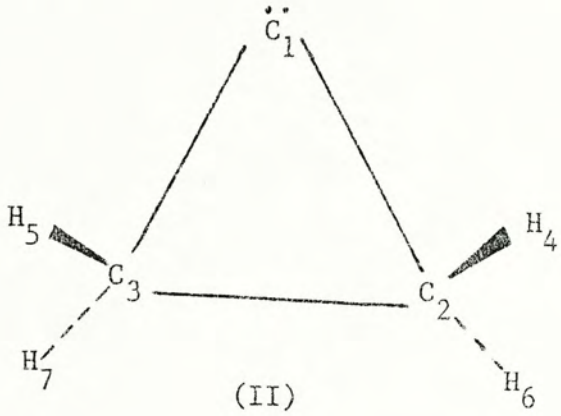
The molecular orbital model used in this study is the MINDO/3 method[6], which has been shown to yield reasonable heats of formation and equilibrium geometries for hydrocarbons. The calclations were carried out on the IBM 3031 computing systems at The Chinese University of Hong Kong.

Referring to the optimization process, it is noted that, for all three molecules, the systems are assumed to have C_{2v} symmetry. The numbering of the atoms is shown in Fig. 1.

The optimized geometries and heats of formations for singlet and triplet states of (I), (II) and (III) are summarized in Tables 1, 2 and 3, respectively. In addition, for comparison, INDO results are included



(I)



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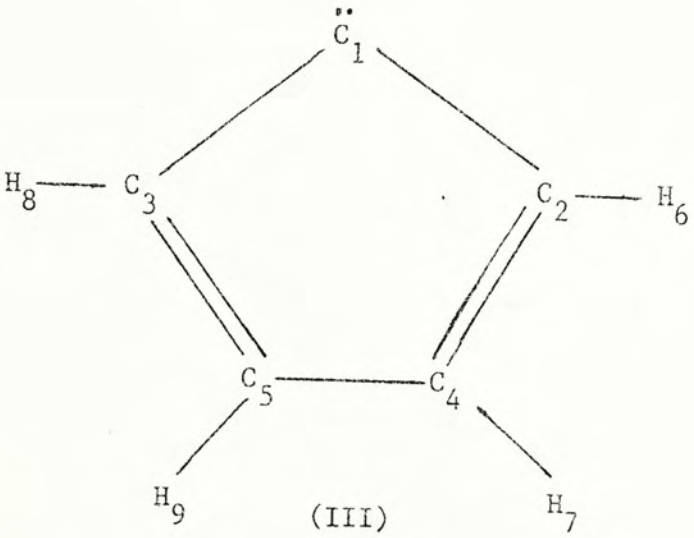


(III)

Fig. 1. Numbering systems for carbenes (I), (II) and (III).

Table 1. Bond lengths (Å), bond angles (degrees), heat of formation and triplet-singlet energy separation in (I) (C_{2v} symmetry). For comparison, INDO results[5] are given in brackets.

	S_o	T_1
C_1-C_2	1.43 (1.40)	1.35 (1.35)
C_2-C_3	1.36 (1.36)	1.53 (1.50)
C_2-H_4	1.10 (1.10)	1.08 (1.10)
C_1-C_2-C_3	61 (61)	56 (56)
C_2-C_1-C_3 (θ)	57 (58)	69 (68)
C_1-C_2-H_4	153 (150)	164 (151)
C_3-C_2-H_4	146 (148)	141 (140)
ΔH_f (kcal/mol)	107	141
ΔE(T-S) (kcal/mol)	34 (81)	

For the reaction of (I) + $H_2 \rightarrow C_3H_4$, ΔH = -48 kcal/mol.

Table 2. Bond lengths (Å), bond angles (degrees), heat of formation and triplet-singlet energy separation in (II) (C_{2v} symmetry). For comparison, INDO results[5] are given in brackets.

	S_o	T_1
C_1-C_2	1.48 (1.45)	1.41 (1.41)
C_2-C_3	1.49 (1.47)	1.61 (1.52)
C_2-H_4	1.10 (1.12)	1.11 (1.12)
C_1-C_2-C_3	60 (60)	55 (57)
C_2-C_1-C_3 (θ)	60 (61)	70 (65)
C_1-C_2-H_4	120 (118)	126 (123)
C_3-C_2-H_4	121 (121)	119 (120)
H_4-C_2-H_6	108	105
ΔH_f (kcal/mol)	96	102
ΔE(T-S) (kcal/mol)	6 (13)	

For the reaction of (II) + $H_2 \rightarrow C_3H_6$, ΔH = -88 kcal/mol.

Table 3. Bond lengths (Å), bond angles (degrees), heat of formation and triplet-singlet energy separation in (III) (C_{2v} symmetry). For comparison, INDO results[5] are given in brackets.

	S_o	T_1
C_1-C_2	1.50 (1.35)	1.42 (1.40)
C_2-C_4	1.35 (1.43)	1.39 (1.37)
C_4-C_5	1.51 (1.42)	1.48 (1.47)
C_2-H_6	1.10 (1.10)	1.09 (1.11)
C_4-H_7	1.10 (1.11)	1.10 (1.12)
C_1-C_2-C_4	110 (78)	101 (92)
C_2-C_1-C_3 (θ)	104 (154)	117 (131)
C_2-C_4-C_5	108 (115)	110 (113)
C_1-C_2-H_6	123 (146)	129 (136)
C_2-C_4-H_7	130 (123)	127 (127)
ΔH_f (kcal/mol)	136	119
ΔE(T-S) (kcal/mol)	-17 (73)	

For the reaction of (III) + $H_2 \rightarrow C_5H_6$, ΔH = - 97 kcal/mol.

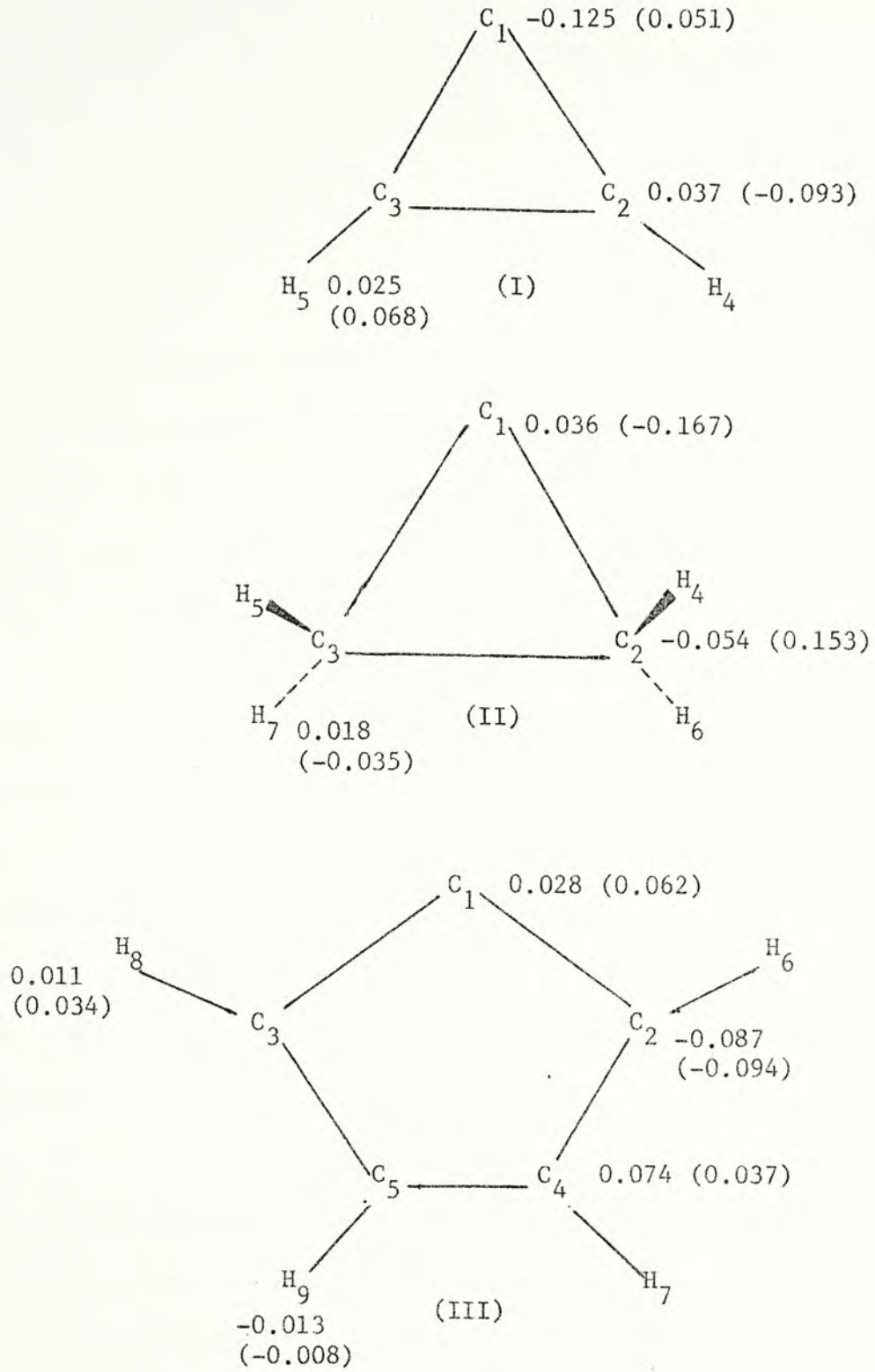


Fig. 2. MINDO/3 formal charges (in unit of electronic charge) for the singlet states of carbenes (I), (II) and (III). Values for the triplet states are given in brackets.

in these tables. The MINDO/3 formal charges for these systems are shown in Fig. 2.

1.3 Discussions

1.3.1 Cyclopropenylidene (I)

In the singlet state of (I), the carbenic centre acquires a negative charge due to the partial population of its empty p_π orbital. The electrophilicity of (I) is very much reduced in comparison to methylene[7,8] because of the conjugation in the aromatic π system of the three-membered ring. The MINDO/3 population of the p_π orbital at C is 0.51, which is consistent with that calculated with CNDO[7]. The conjugation is reflected in orbital energies (eV): the LUMO of (I) is 1.90, and the energy of HOMO, which correspond to the lone pair, is -8.67. This large splitting between the HOMO and LUMO in (I) causes the triplet state to be much higher in energy than the singlet[3,7,9].

The MINDO/3 heat of formation for (I) is 107 kcal/mol, in fair agreement with that of Pople et al[9], 113 kcal/mol. According to Kollmar[7], since ring strain and inductive effects for both (I) and (II) should be similar, the difference in heats of reaction for the hydrogen insertions of (I) and (II) (see Tables 1 and 2) is a good measure for the aromatic stabilization of (I). Thus the MINDO/3 value for this quantity is 40 kcal/mol, in good agreement with Kollmar's estimate of 45 kcal/mol, using ab initio methods.

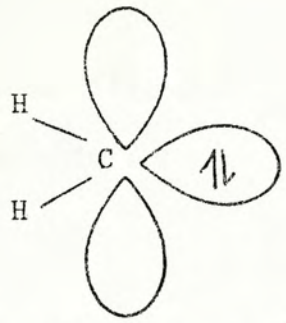
The MINDO/3 heats of reaction for hydrogen insertions of methylene and (I) are -107 and -48 kcal/mol, respectively. The difference of these

two values, 59 kcal/mol, may be taken as a measure of the stability of the carbenic carbon of (I) relative to methylene. This is in fair agreement with the values of Kollmar[7] (70 kcal/mol) and Pople et al[10] (74 kcal/mol).

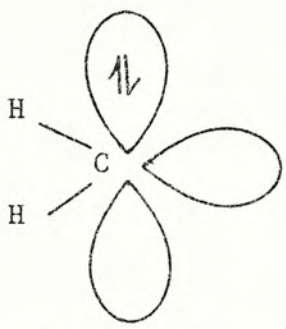
The aromatic conjugation of (I) is also reflected in its structure in the singlet state. The optimum structure has single bonds of 1.43 Å and double bond of 1.36 Å. Compared with those in cyclopropene (MINDO/3), 1.48 and 1.32 Å, respectively, the single bonds are shortened by 0.05 Å, while the double bond is stretched by 0.04 Å.

Simons et al[11] found that at least two configurations (A and B in Fig. 3) are required to describe the lowest $^1A_1$ state of methylene. However, for (I), the analogous B configuration would not be important for the description of the lowest singlet state, since this configuration has anti-aromatic character[12]. On the other hand, for the description of the triplet state of (I), other low-energy excited triplet configuration may be important.

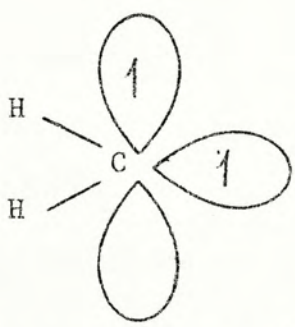
In the triplet state of (I), an electron is promoted from HOMO to LUMO, which is of a_2 symmetry, consisting orbitals $p_{\pi 2}$ and $p_{\pi 3}$ only. Thus the C_2-C_3 bond is weakened. The ΔE (T-S) is 34 kcal/mol; that calculated with INDO[5] is much higher, 81 kcal/mol. This relative high energy separation between the singlet and triplet state is mainly due of the occupation of the LUMO, which is antibonding as far as C_2-C_3 is concerned. Also, in the triplet state, the delocalization of the two π electrons is retarded. Hence the C_1 charge in the triplet state (0.05) is more positive than that in the singlet state (-0.13).



Configuration A ($^1A_1$)



Configuration B ($^1A_1$)



Configuration C ($^3B_1$)

Fig. 3. The three lowest-energy configurations of methylene.

1.3.2 Cyclopropylidene (II)

In the singlet state of (II), through hyperconjugation, electron flows from the carbenic centre to the other two carbenes, resulting in a charge of 0.04 for C_1 and -0.05 for C_2 and C_3. The MINDO/3 population for the p_π orbital at C_1 is 0.13, much lower than that for (I) (0.51), hence it is expected that (II) is much more electrophilic than (I).

The energy of LUMO of (II) is 0.10 eV, while the energy of HOMO, the lone pair, is -8.67 eV. In view of this large splitting, it is not surprising that the ground state of (II) is a spin singlet. The energy of the lone pairs in the two three-membered ring carbenes, (I) and (II), are similar, while the lone pair of (III), is of lower energy. It is because of the larger s character in the lone pair of (III).

The stabilization of (II) with respect to methylene is about 20 kcal/mol, Kollmar[7] has suggested that hyperconjugation contribrtes only 7 kcal/mol to the stability of (II). The optimum structure of (II) has C-C bonds 1.48 and 1.49 Å, while that in cyclopropane is 1.49 A. The C_1-C_2 and C_1-C_3 bonds are shortened by 0.01 Å, while the C_2-C_3 bond remains nearly the same. This shortening reflects the hyperconjugation interaction. But this interaction is rather weak, as can be observed from the small change in bond lengths.

In the triplet state of (II), the shortening in C_1-C_2 and C_1-C_3 bonds are more pronounced, due to the promotion of electron from HOMO to a π system consisting mainly of $p_{\pi 1}$ orbital, removing 0.7 electron from C_2 and C_3 to $p_{\pi 1}$. This accounts for the negative charge on C_1 and the hydrogens in triplet state.

Going from the singlet to the triplet state for (I), aromaticity

is destroyed. But for (II), aromatic stability is clearly not a factor, therefore a much smaller difference in ΔH_f between the triplet and singlet states is resulted.

1.3.3. Cyclopentadienylidene (III)

Though INDO[5] calculation predicts a singlet ground state for (III), MINDO/3 study reveals a triplet ground state. The latter is supported by experimental evidence and some previous calculations.

According to the EHMO calculation of Hoffmann[3,13], the LUMO (III) has the correct symmetry for interaction with the methylene $p_{\pi 1}$, while the $p_{\sigma 1}$ (lone pair) orbital has also been stabilized by the bending at the carbenic centre, with the $p_{\sigma 1}$ orbital lying 0.13 eV below the delocalized $p_{\pi 1}$. This small splitting[4] leads to a triplet ground state for (III).

In 1964, Wasserman et al[14] have discovered that when diazocyclopentadienylidene (CpN_2) is photolyzed in a solid medium, such as hexafluorobenzene or hexachlorobutadiene at 77° or 4°K, a triplet ESR spectrum can be observed, which is attributed to the ground state of (III). Analysis of the ESR spectrum reveals that one unpaired electron is in the π system and the other is localized in an in-plane orbital at C_1.

Examining the structure of (III) given in Table 3, it is seen that, in the singlet state, since the lone pair lies in the molecular plane and there are four π electrons in the system, extensive delocalization of the π electrons is not expected. The single and double bonds are clearly discernible in this state. However, in the triplet state, with one electron in the p_π orbital of C_1, delocalization effect causes the five C-C bonds to have similar lengths, and lower energy for the system. This delocalization effect is also apparent when the formal charges of III (Figure 2) are

examined. In the singlet state, C_1 has a charge of 0.03. In the triplet state, the lone electron in the p_π orbital of C_1 flows toward the π system of the diene, leading to a more positive charge, 0.06. Also, MINDO/3 results indicate that there is 0.21 electron, in the p_π orbital of C_1 in the singlet state of (III). Thus its electrophilicity is much greater than that of (I) which has 0.51 electron in the same orbital.

It is worth noting that the INDO[5] and ab initio[15] calculations for the singlet state of (III) lead to a "cumulenic" structure for (III):

Finally, it is mentioned that all three cyclic carbenes, upon going from singlet to triplet, the apex angle (θ in Tables 1, 2, and 3) increases by about 10^{o}. This is because all three carbenes have the lone pair lying in the molecular plane.

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PART 2

THE NON-LEAST-MOTION INSERTION OF CYCLIC CARBENES

2.1 Introduction

A thermal reaction for which the most symmetric path is forbidden may proceed in a concerted way if the system follows a low-symmetry path.[1] Theoretically studied examples for reactions which proceed with a low energy barrier along a low-symmetry path include the insertion of methylene into hydrogen[2] and into methane[3], the insertion of vinylidene into hydrogen,[4] chlorlmethylene[5] into hydrogen and the addition of methylene to ethylene[6].

All these calculations predict similar low-energy, low-symmetry path for the reactions characterized by the approach of a bond of the substrate to the empty p_π orbital of the singlet carbene from above the molecular plane. These reactions represent an illustration for the frontier orbital model[7].

The H_2 insertions of cyclopropenylidene (I), cyclopropylidene (II) and cyclopentadienylidene (III) are studied in this work with the MINDO/3 method. For all three, two well defined phases can be distinguished along the path of the concerted reaction: (i) The H_2 molecule approaches the carbene from above and a three-centre bond is formed between the occupied hydrogen MO and the empty p_π orbital of the carbene in the electrophilic phase of the reaction; (ii) in the second phase of the reaction the H_2 molecule rotates to the final tetrahedral arrangement. The second phase is coupled with the simultaneous increase of the H-H bond length; it is the nucleophilic phase of the reaction, during which the antibonding MO of

the hydrogen molecules is populated with the lone pair electron of the carbene. But in (I)[8], the carbenic centre is stabilized by conjugation in the aromatic three-membered ring, hence the empty p_π orbital of the carbene is partially populated. In (III), there is a diene conjugated with the carbenic centre, which allows a redistribution of electron population during the electrophilic phase. All these have immense effect on the electronic structures, making the patterns of reactions quite different from one another. Furthermore, the electrophilic phase of (III) is complicated by the presence of a diene, but this phase can be well defined by the change in electron density of the hydrogen molecule.

2.2 Method of Calculation

In calculating the one-dimensional energy profiles of (I) + H_6-H_7, (II) + H_8-H_9, (III) + H_{10}-H_{11}, the mean C-H distance, $\bar{r}$, or $\frac{1}{2}$(C-H_a + C-H_b), where C is the carbenic carbon, and H_a and H_b the atoms of reacting hydrogen molecule, was chosen as the reaction coordinate, while all other geometrical parameters were optimized.

The two-dimensional energy contour maps for the three non-least-motion reactions were obtained in the following way: for different given H_a-H_b values, $\bar{r}$ was varied over a wide range (0.1-4.5 Å), while all other structural parameters were optimized. The reacting hydrogen atoms could move freely in the space to attack the carbenic centre in a most favourable way above the carbene molecular plane.

2.3 Results and Discussion

2.3.1. The Insertion of Cyclopropenylidene into Molecular Hydrogen

The calculated heat of reaction for (I) + H_2 → cyclopropene is -48 kcal/mol. This value is acceptable since the MINDO/3 overestimations of the stability of small ring (I) and cyclopropene cancel each other out.

The one-dimensional energy profile and the two-dimensional energy contour map for the reaction are shown in Figs. 1. and 2, respectively. The critical region of the two-dimensional contour map is expanded and shown in Fig. 3.

For $\bar{r} > 3.0$ Å, there is no attractive force operating between the two interacting molecules. Just before interaction takes place, the inserting angle α is 85° (Fig. 4) with the core resonance energy, E_r, of the hydrogen σ bond (H-H $\sim$ 0.75 Å) being -194 kcal/mol.

In the range of 3.0 Å > $\bar{r}$ > 1.9 Å, weak interaction between the two molecules begins. The total energy of the system increases by 5 kcal/mol, but the change in the electronic distribution in atoms of (I) is small. [There is a flow of 0.012 electron from H_2 to the canbene molecule.] A point of interest in this region is at $\bar{r}$ = 2.2 Å, where the angle α drops from 85° to 31° when $\bar{r}$ reaches 1.9 Å, while the overall change in the geometry of (I) is small.

In the range of 1.9 Å > $\bar{r}$ > 1.3 Å, the insertion angle remains in the region $30\text{-}35^{\circ}$. Also, there is a flow of electron from C_1 to C_2 and C_3, strengthening the C_2-C_3 double bond and enhancing the insertion of the carbenic p_π orbital into the molecular hydrogen. Around the end of this range ($\bar{r}$ = 1.35 Å), there is a flow of 0.04 electron from H_2 to the carbene system, forming a three-centre bond in the process. This concludes the electrophilic phase of the reaction. At this point, the core resonance

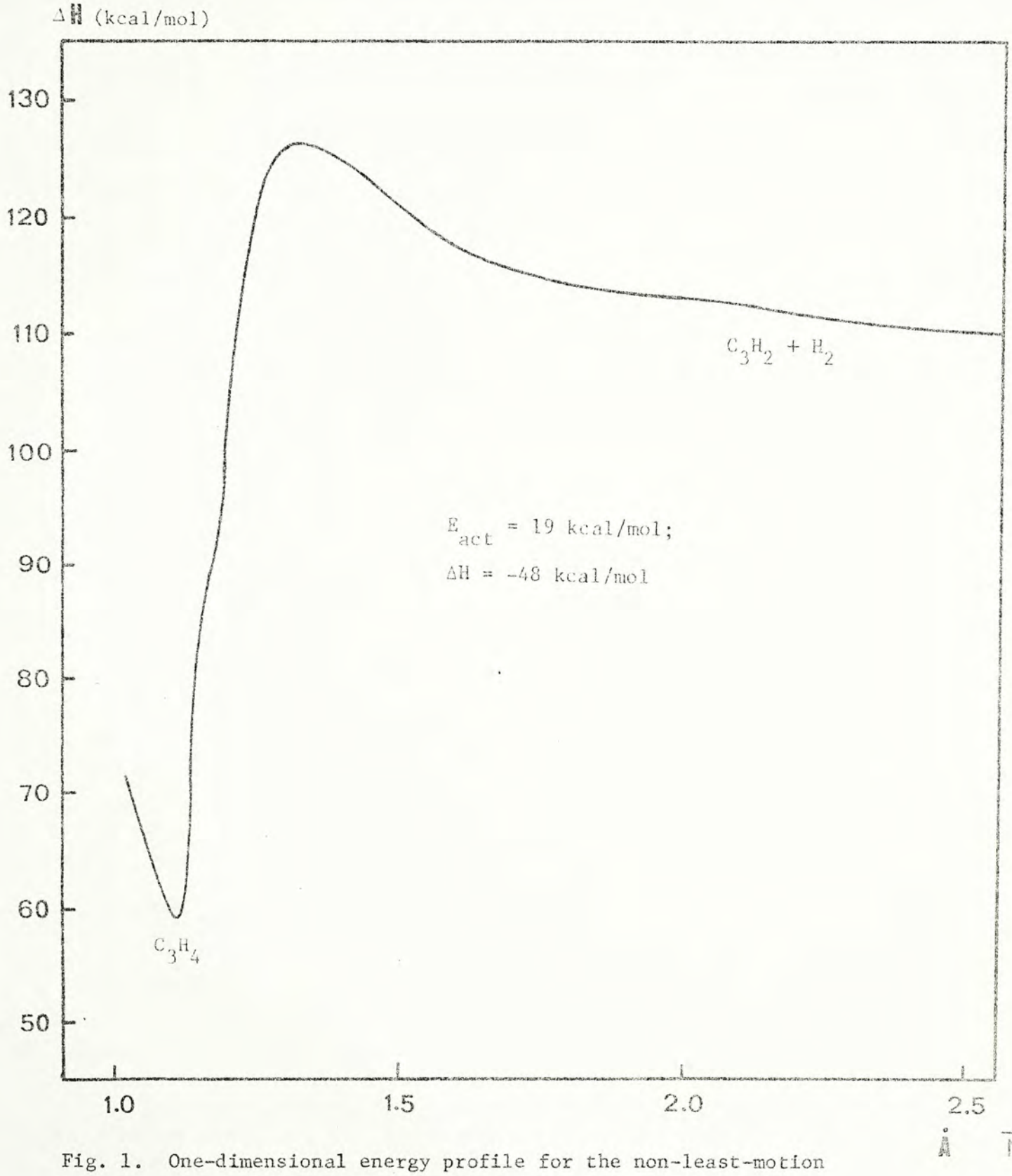


Fig. 1. One-dimensional energy profile for the non-least-motion reaction of cyclopropenylidene + H_2.

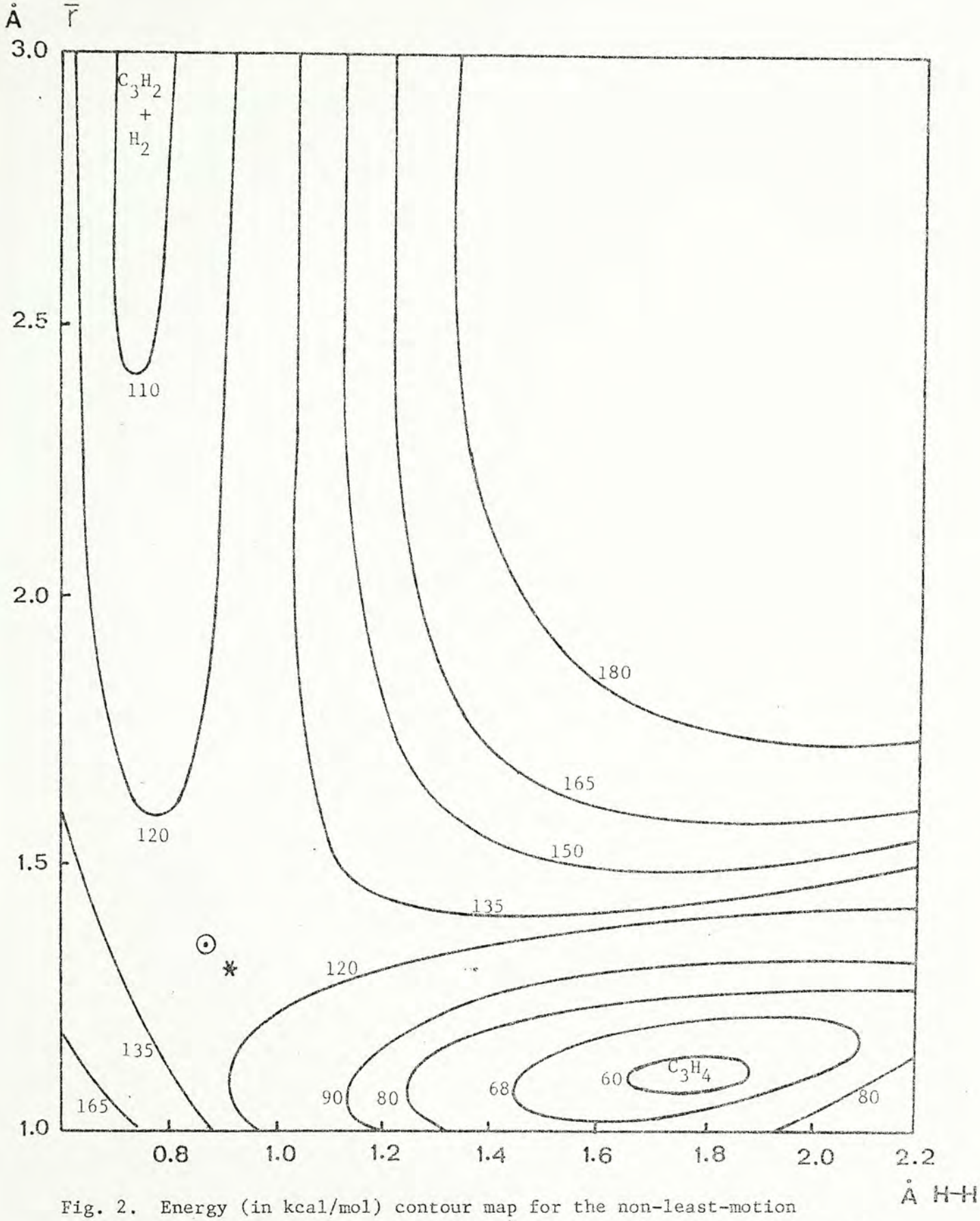


Fig. 2. Energy (in kcal/mol) contour map for the non-least-motion reaction of cyclopropenylidene + H_2. The asterisk and ⊙ denote the saddle point and the turning point, respectively.

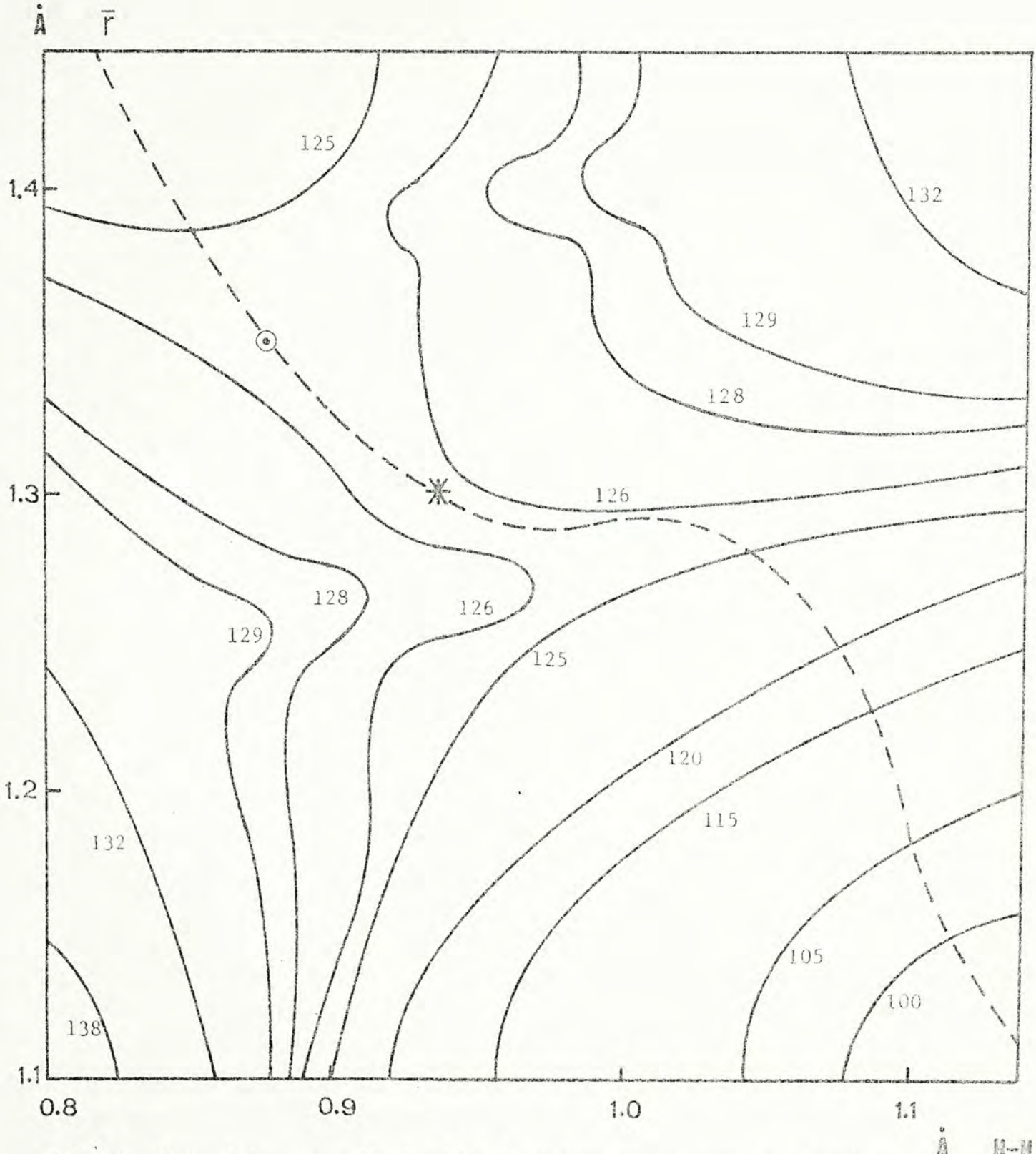


Fig. 3. Expanded energy (in kcal/mol) contour map around the saddle point for the non-least-motion reaction of cyclopropenylidene + H_2. The asterisk and ⊙ denote the saddle point and the turning point, respectively.

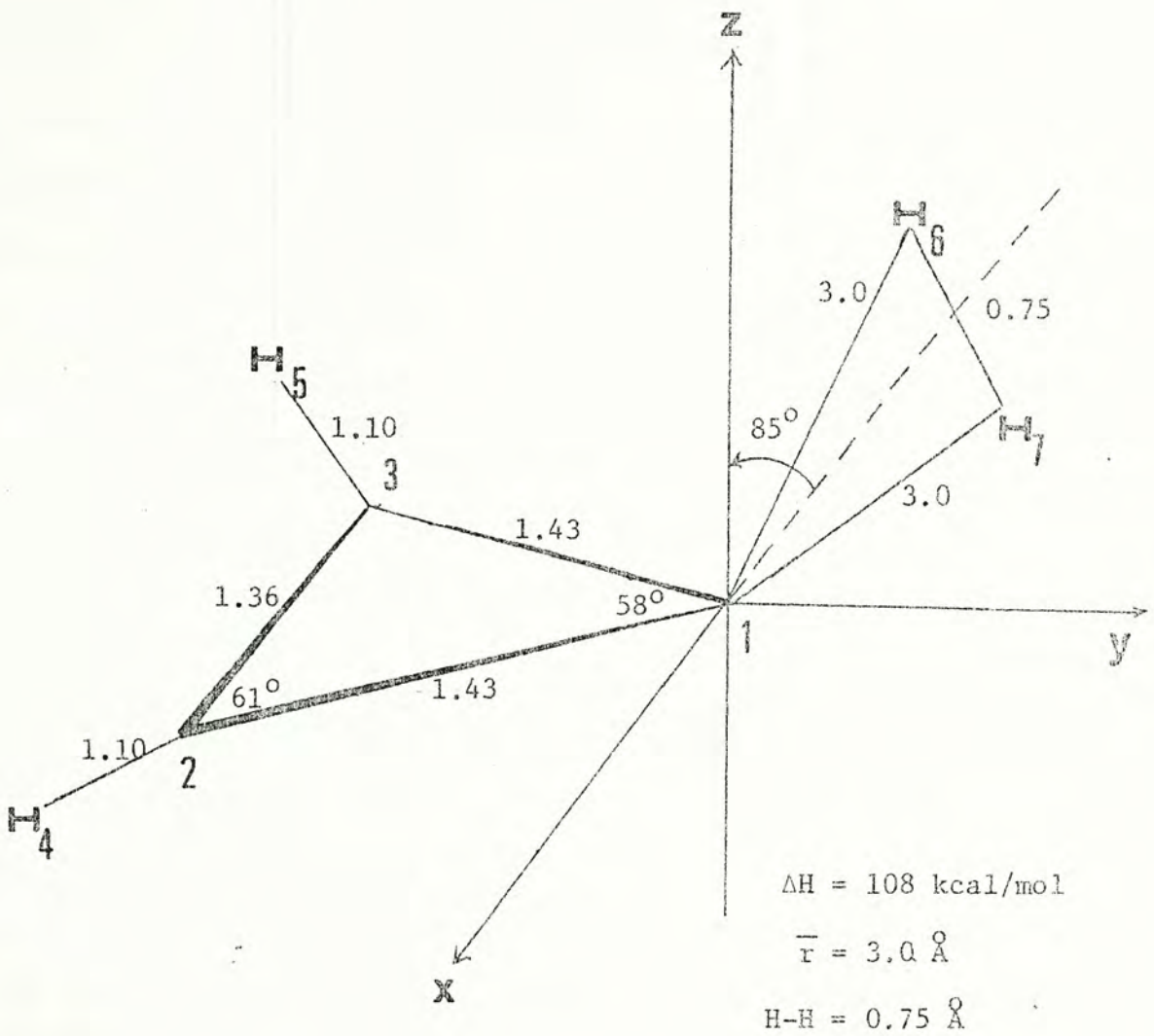


Fig. 4 Geometrical arrangement for cyclopropenylidene + H_2 in the beginning of the non-least-motion reaction. Distances are in Å. The inserting angle α is the angle between the line joining the mid-point of H-H bond and the carbenic centre and the line perpendicular to the molecular plane through this centre. Here $\alpha = 85^{\circ}$.

energy E_r of the hydrogen σ bond (H-H $\sim$ 0.87 Å) is -93 kcal/mol and that of the C-H bond is -117 kcal/mol.

After this point, the nucleophilic phase commences; this is the "turning point" of the reaction. As can be seen in Fig. 3, almost as soon as this phase begins, at $\bar{r}$ = 1.31 Å, the transition state is reached, the structure of which is shown in Fig. 5. The ΔH for this point is 126 kcal/mol, yielding an relatively high activation energy of 19 kcal/mol for the reaction. Such a small value of $\bar{r}$ for the transition state is rather untypical for this kind of reactions (usually $\bar{r}$ is around 2.0-2.5 Å [2,4]). This is mainly due to the high p_π population of 0.51 at C_1 for the carbene (section 1.3.1). Due to this delay for the formation of the transition state, the geometrical structures of the transition state and the product are rather similar.

In the nucleophic phase, the insertion angle α steadily increases from $\sim 30^\circ$ to $\sim 90^\circ$ and there is a rapid drop in total energy (Fig. 1). Also, there is a flow of electron from the lone pair of the carbene to the σ^* orbital of the hydrogen molecule; the charge of C_1 increases from -0.12 to 0.11 and that of H_2 decreases from 0.04 to -0.14 in this phase. Specifically, at $\bar{r}$ = 1.18 Å, the two C-H bonds become identical and the H-H bond is almost completely broken, with E_r being -3 kcal/mol. Beyond $\bar{r}$ = 1.15 Å, the H-H separation starts to replace $\bar{r}$ as the reaction coordinate.

Finally, a brief comparison between the present study and those of other H_2 insertion is made. First of all, the present result is in good agreement with that of Kollmar[8], who also studied this reaction. However, while the H_2 insertions of methylene[2], vinylidene[4] and (I) are qualitatively similar , there are definite quantitative differences. The most important

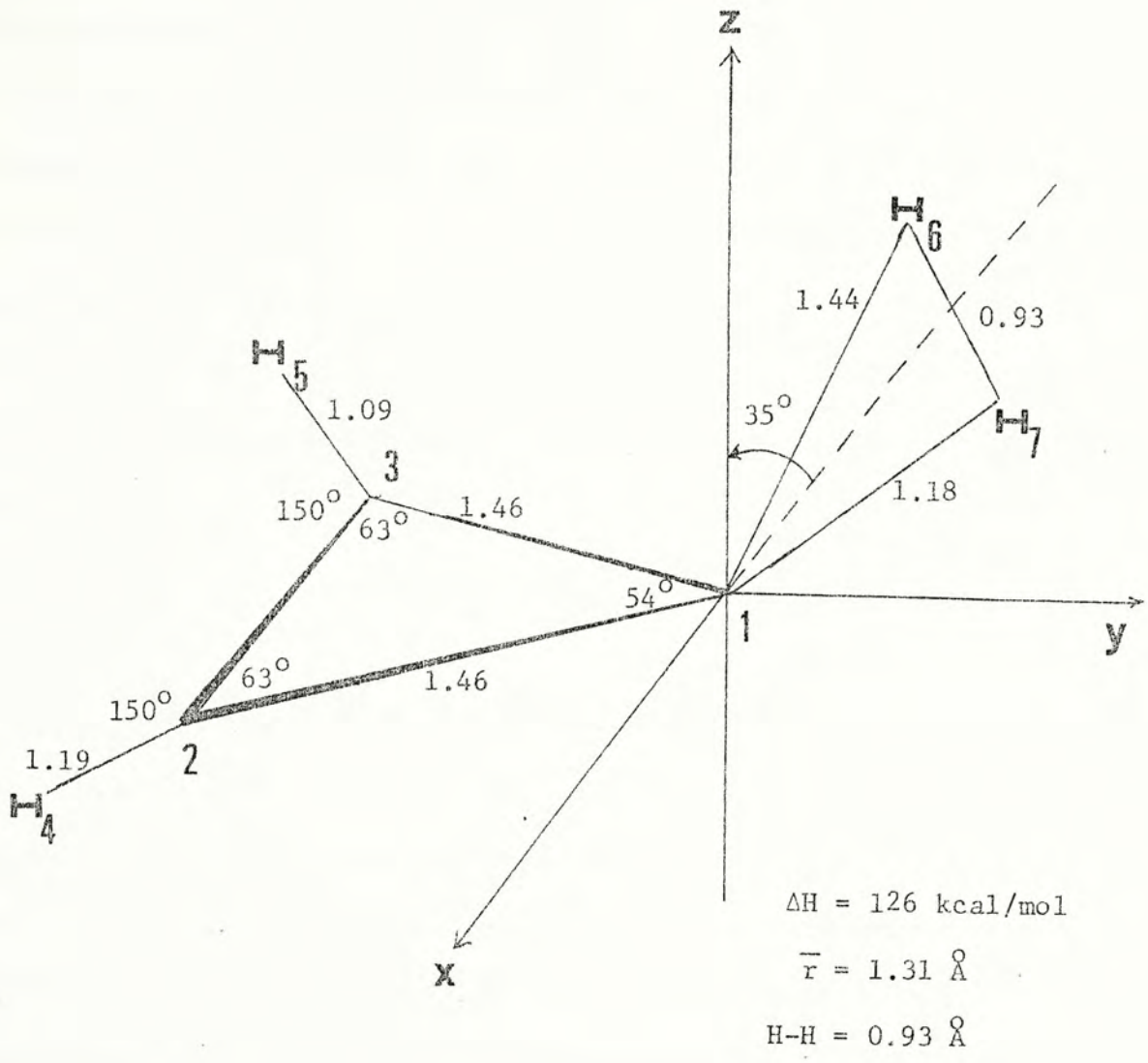


Fig. 5 Geometry of the transition state for the non-least-motion reaction of cyclopropenylidene + H_2. Distances are in Å.

ones are that H_2 + (I) has a relatively high activation energy of 19 kcal/mol [that for H_2 + vinylidene is 5-10 kcal/mol[4]] and that the transition state is formed at a rather late stage of the reaction: $\bar{r}$ = 1.31 Å [those for H_2 + vinylidene and H_2 + methylene are ∿2.4]. As mentioned before, the p_π orbital at C_1 of (I), due to delocalization of π electrons, has a high population of 0.51 electron. This hinders the flow of electron from the H_2 molecule toward the carbene, thus delaying the formation of the transition state. When the two interacting molecules get close enough for the electron transfer from H_2 to carbene, there is a corresponding flow of electron from C_1 to C_2 and C_3, thus localizing the C_2-C_3 π bond and destroying the aromatic character of the carbene system (C_1-C_2 and C_1-C_3 are lengthened). Hence, the activation energy for the reaction is exceptionally high.

2.3.2 The Insertion of Cyclopropylidene into Molecular Hydrogen

The MINDO/3 heats of reactions for (II) + H_2 → cyclopropane and methylene + H_2 → CH_4 are -88 and -107 kcal/mol, respectively. The difference of these two values, 19 kcal/mol, may be taken as a measure of the stability of the carbenic carbon of (II) relative to methylene. Referring to this stability, Kollmar[8] has estimated that the hyperconjugation interaction in (II) accounts for 7 kcal/mol of its stabilization relative to methylene.

The one-dimensional energy profile and the two-dimensional energy contour map for the reaction (II) + H_2 are shown in Figs. 6 and 7, respectively.

In the region $\bar{r}$ > 2.5 Å, there is very weak interaction between

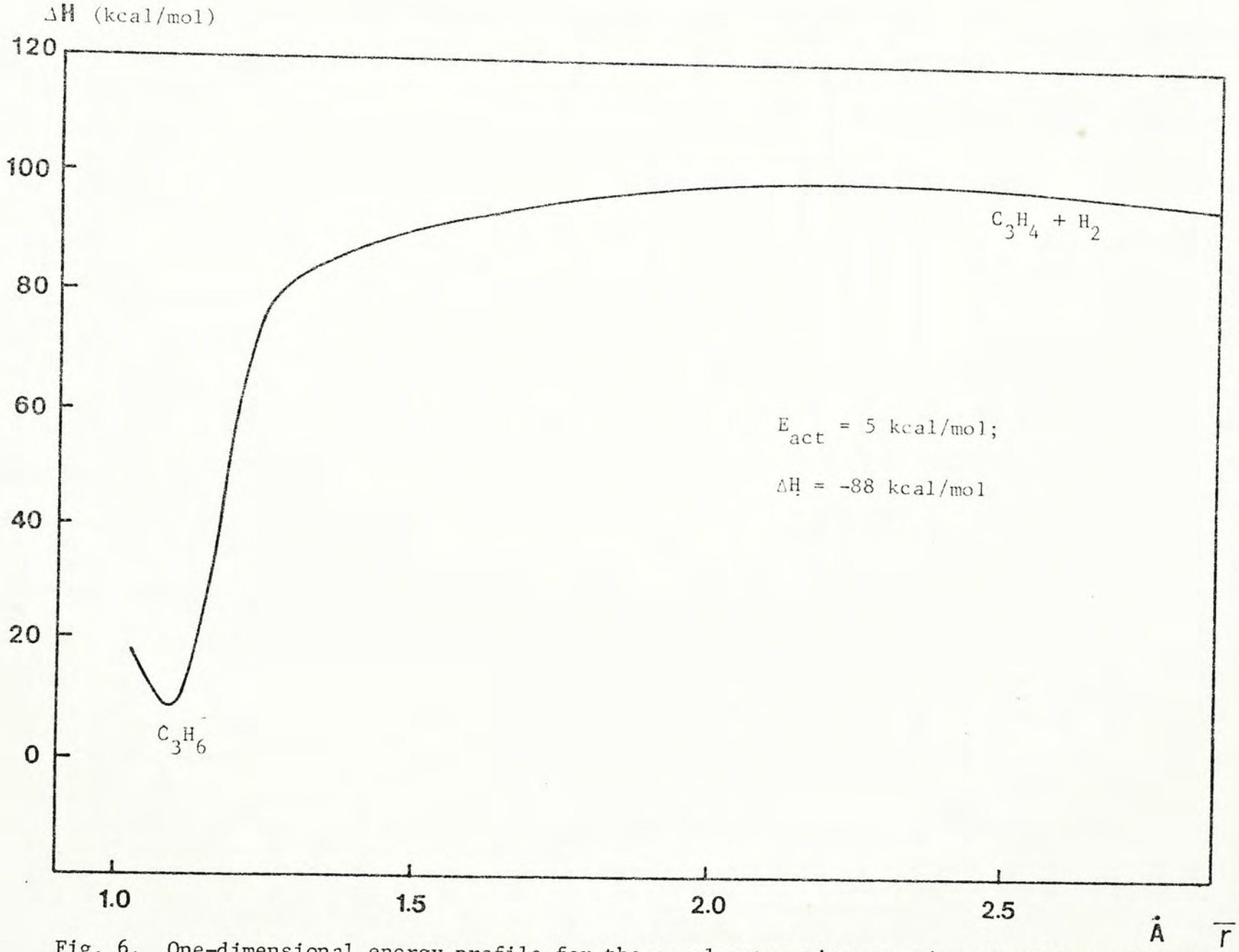


Fig. 6. One-dimensional energy profile for the non-least-motion reaction of cyclopropylidene + H_2.

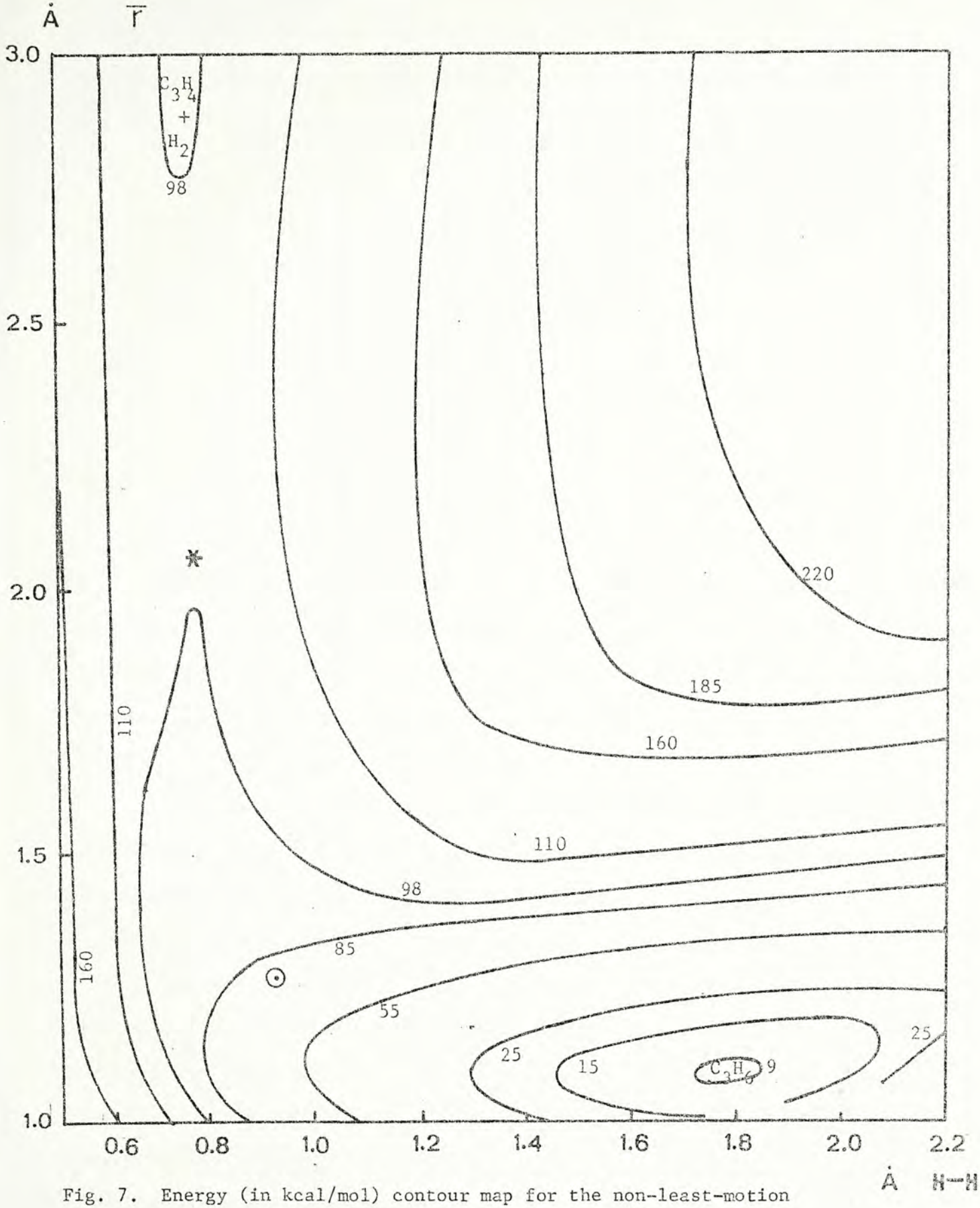
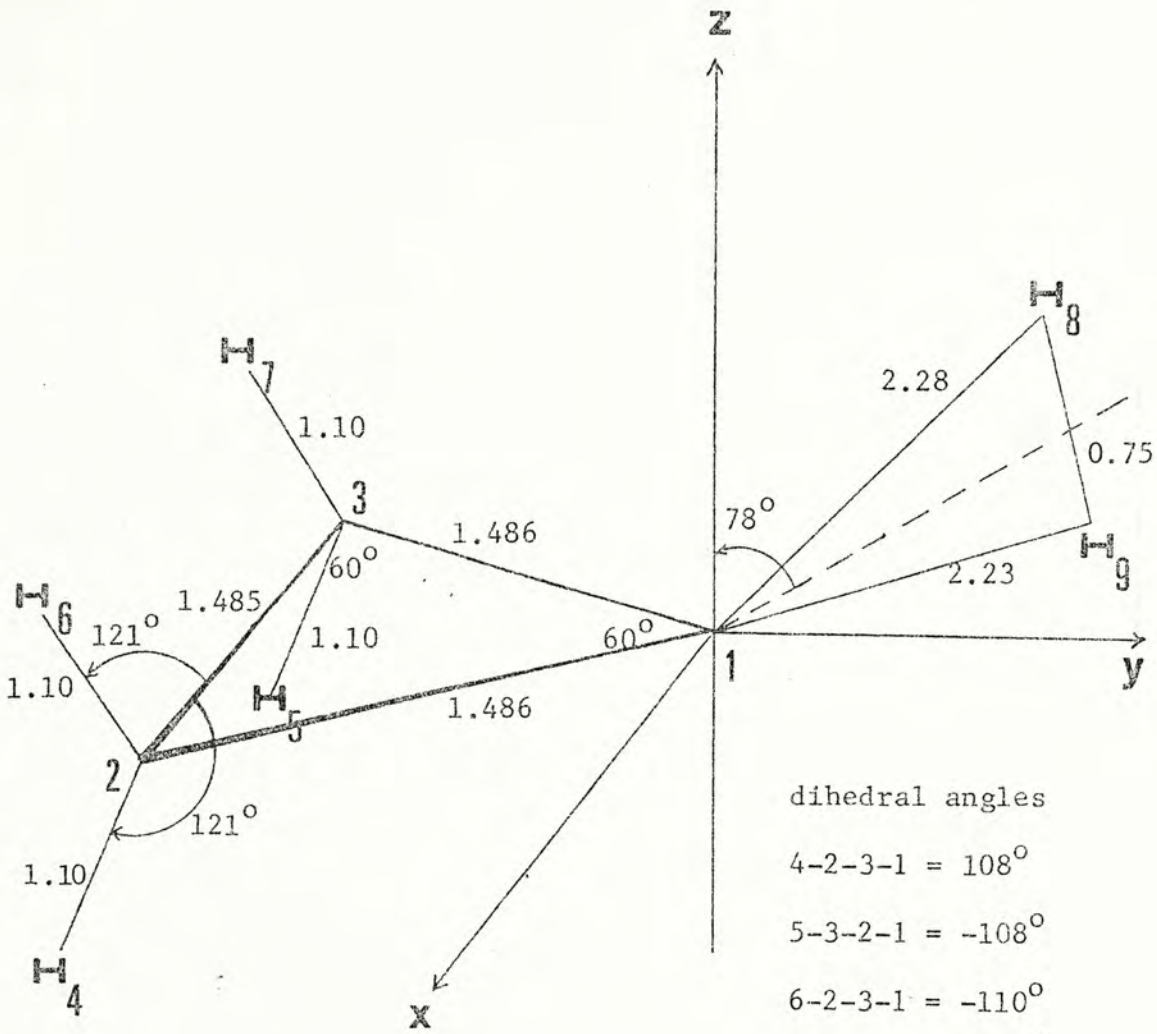


Fig. 7. Energy (in kcal/mol) contour map for the non-least-motion reaction of cyclopropylidene + H_2. The asterisk and ⊙ denote the saddle point and the turning point, respectively.

the carbene and the H_2 molecule. When the reactants get closer to $\bar{r} \sim 2.45$ Å, a greater interaction begins at an inserting angle 78° (Fig. 8) with an increase in energy of the system by 3 kcal/mol. There are only small changes in the geometrical and electronic structures for (II) at this moment.

From $\bar{r} \sim 2.45$ to $\bar{r} \sim 1.28$ Å, the energy of the system rises to a peak of 102 kcal/mol at $\bar{r} \sim 2.05$ Å, yielding an activation energy of about 5 kcal/mol. This is the transition state of the reaction, as shown in Fig. 7. The geometry of this activated complex is shown in Fig. 9, where it is seen that the inserting angle of the activated complex has decreased to 57°. At this point, the H_2 molecule is still intact, with E_r being -188 kcal/mol and separation 0.76 Å. Although only 0.01 electron is donated from H_2 molecule, the intramolecular redistribution of (II) enables the carbenic centre is increase population by 0.026. The electronic structure of transition state resembles closely to that of the reactant.

From the transition state to $\bar{r} \sim 1.28$ Å, the energy of the system decreases steadily down to 82 kcal/mol, with the inserting angle remaining at around $25^\circ \sim 30^\circ$. The formation of the three-centre bond between p_π orbital of carbenic centre and H_2 is evident. The smallness of the activation energy for this reaction and the facile formation of the three-centre bond can be attributed to the "emptiness" of the p_π orbital of the carbenic centre of (II) (0.13 electron). Before $\bar{r} \sim 1.4$ Å, the reaction coordinate is essential $\bar{r}$, the average of C-H distances. The two H atoms bear different charges with the two different C-H distances (E_r of "bonds" C_1-H_8 and C_1-H_9 are -53 kcal/mol and -151 kcal/mol, respectively). At the end of this phase ($\bar{r} \sim 1.28$ Å), there is only 0.18 electronic charge transfered to the carbene from the H_2 molecule. But the carbenic carbon

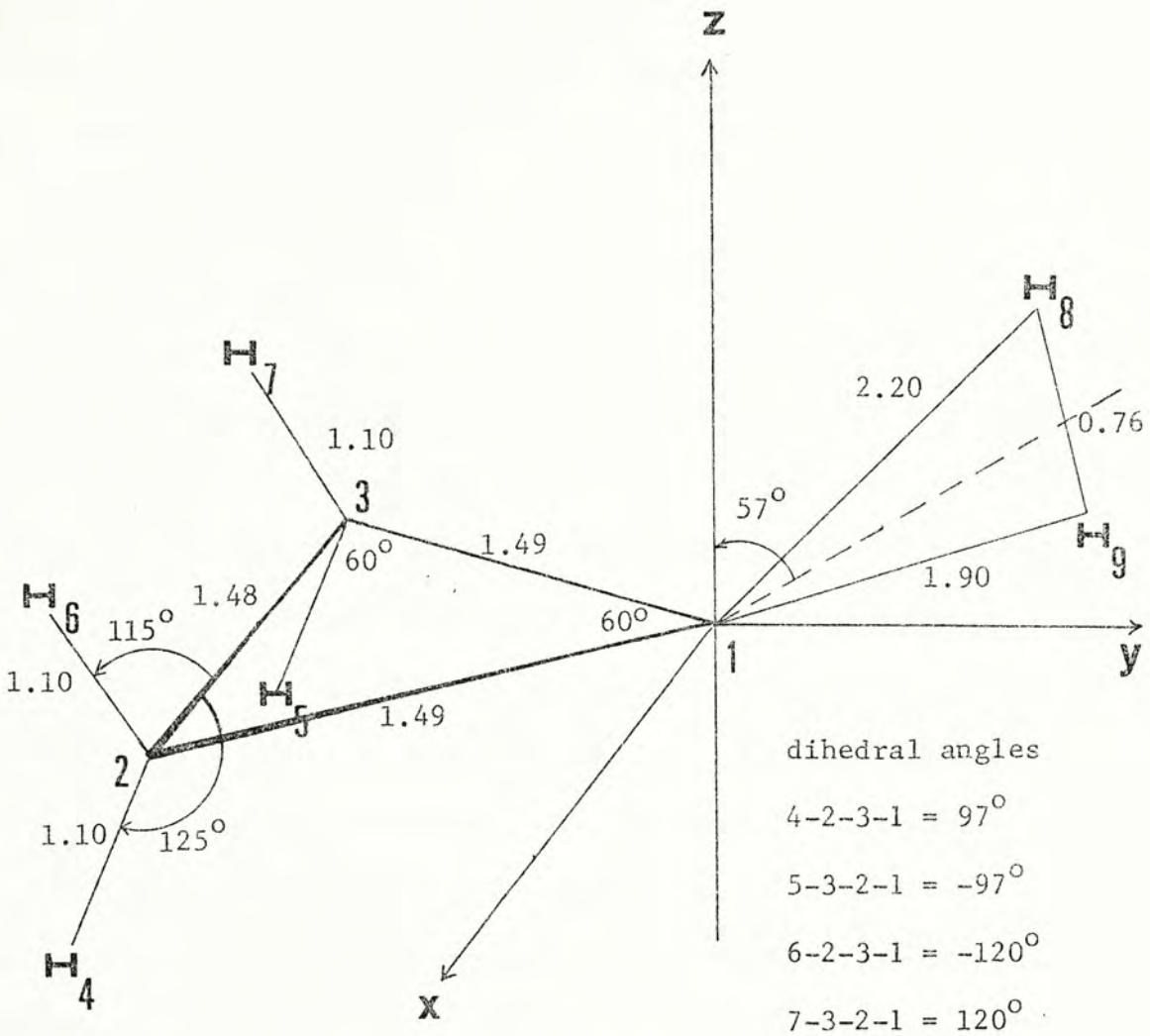


ΔH = 101 kcal/mol

$\bar{r}$ = 2.25 Å

H-H = 0.75 Å

Fig. 8 Geometrical arrangement for cyclopropylidene + H_2 in the beginning of the non-least-motion reaction. Distances are in Å.



ΔH = 101 kcal/mol

$\bar{r}$ = 2.05 Å

H-H = 0.76 Å

Fig. 9 Geometry of the transition state for the non-least-motion reaction of cyclopropylidene + H_2. Distances are in Å.

bearing a charge -0.22 has acquired more than 0.25 electron during this phase. Thus this phase of reaction is an electrophilic one. The structure of the system at the turning point ($\bar{r}$ = 1.28 Å) is a distorted one, with C_2-C_3 bond (1.51 Å) being longer than C_1-C_2 (1.46 Å) and C_1-C_3 (1.47 Å) bonds and the inserting angle rising to 40°. This is called the turning point of the reaction as, after this point, the charge on the carbenic centre begins to rise sharply from -0.22 to 0.02 for the product. Hence the second phase is a nucleophilic one.

Fig. 6 shows that the nucleophilic phase is characterized by a rapid fall of the energy for the system and the H_2 bond strength. The strength of the two new C-H bonds increases sharply (E_r from -158 kcal/mol at $\bar{r} \sim 1.28$ Å to about -259 kcal/mol for the product), at the same time diminishing their difference to form two equivalent bonds. The energy of the system decreases by 70 kcal/mol within a change of 0.2 Å for $\bar{r}$, and the inserting angle of H_2 rotates from 40° to 85° within a change of 0.1 Å for $\bar{r}$. At the same time, the H-H distance lengthens from 0.92 Å to greater than 1.75 Å, accompanied by the rise of E_r of H_2 bond to a positive value. This is the result of the nucleophilic interaction of the carbenic centre in which the lone pair of the carbene interacts with the σ^* orbital of the hydrogen molecule.

The H_2 insertion of (II) is very similar to that of methylene: it has very well defined electrophilic and nucleophilic phases. The positions of transition states and turning points for the two reactions are very similar. The greater electrophilicity of the "empty" carbene p_π orbital of (II) with respect to (I) accounts for the lower energy barrier for the reaction of (II) + H_2. The carbene insertion process can be hindered by lowing the electrophilicity of the carbene p_π orbital but it cannot be

hindered by lowering the nucleophilicity of the carbene lone pair, since the second phase of the reaction is not rate-determining[2].

2.3.3. The Insertion of Cyclopentadienylidene into Molecular Hydrogen

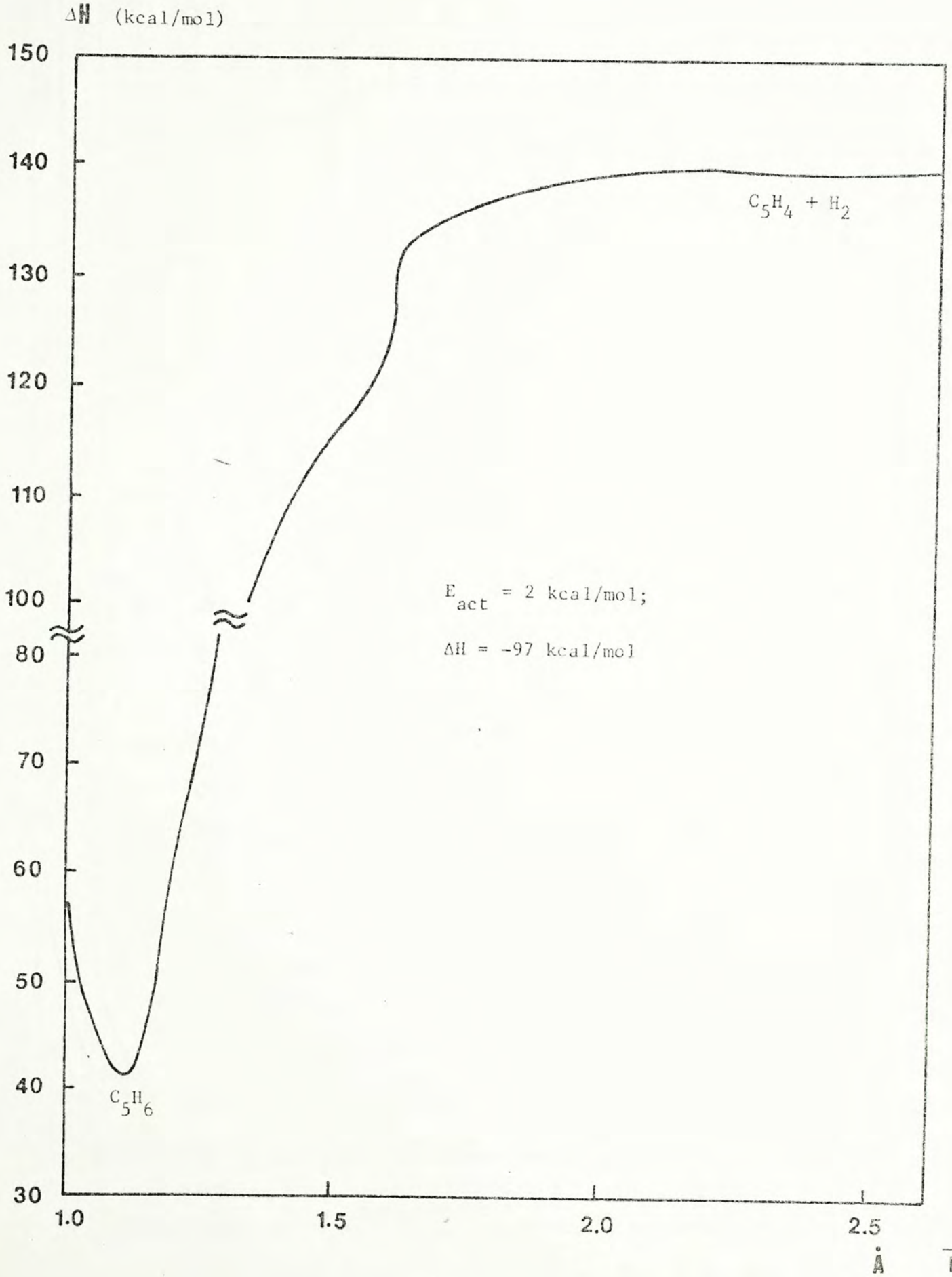
Although the ground state of cyclopentadienylidene (III) is a spin triplet, its prototype insertion proceeds in the singlet state. Since the diene system can serve as a reservoir for electrons, intramolecular redistribution of electrons should affect the reaction path greatly. In particular, it should make the electron density on the carbenic centre vary in a pattern very different from that of (I) and (II). As seen in the previous two sections, in the H_2 insertions of (I) and (II), the electrophilic and nucleophilic phases are well defined from the smooth or sudden change in the charge of the carbenic centre during the reaction. However, for the H_2 insertion of (III), the charges of the hydrogens, instead of that of the carbenic centre, define the two phase more clearly.

For the reaction of (III) + H_2 → cyclopentadiene, the MINDO/3 heat of reaction is 97 kcal/mol. Thus the stability of carbene (III) relative to methylene is 10 kcal/mol. The one-dimensional energy profile and the two-dimensional energy contour map for the reaction are shown in Fig. 10 and 11, respectively.

For the region $\bar{r} > 2.5$ Å, there is only weak interaction between the reactants; the energy has only risen by 2 kcal/mol. The only significant change is the decrease of inserting angle α from 72° at $\bar{r} \sim 3.0$ Å to 34° at $\bar{r} \sim 2.5$ Å.

During the range of $2.57 > \bar{r} > 1.44$, the energy of the system reaches a maximum of 140 kcal/mol at $\bar{r} = 2.25$ Å, yielding an activation

Fig. 10. One-dimensional energy profile for the non-least-motion reaction of cyclopentadienylidene + H_2.



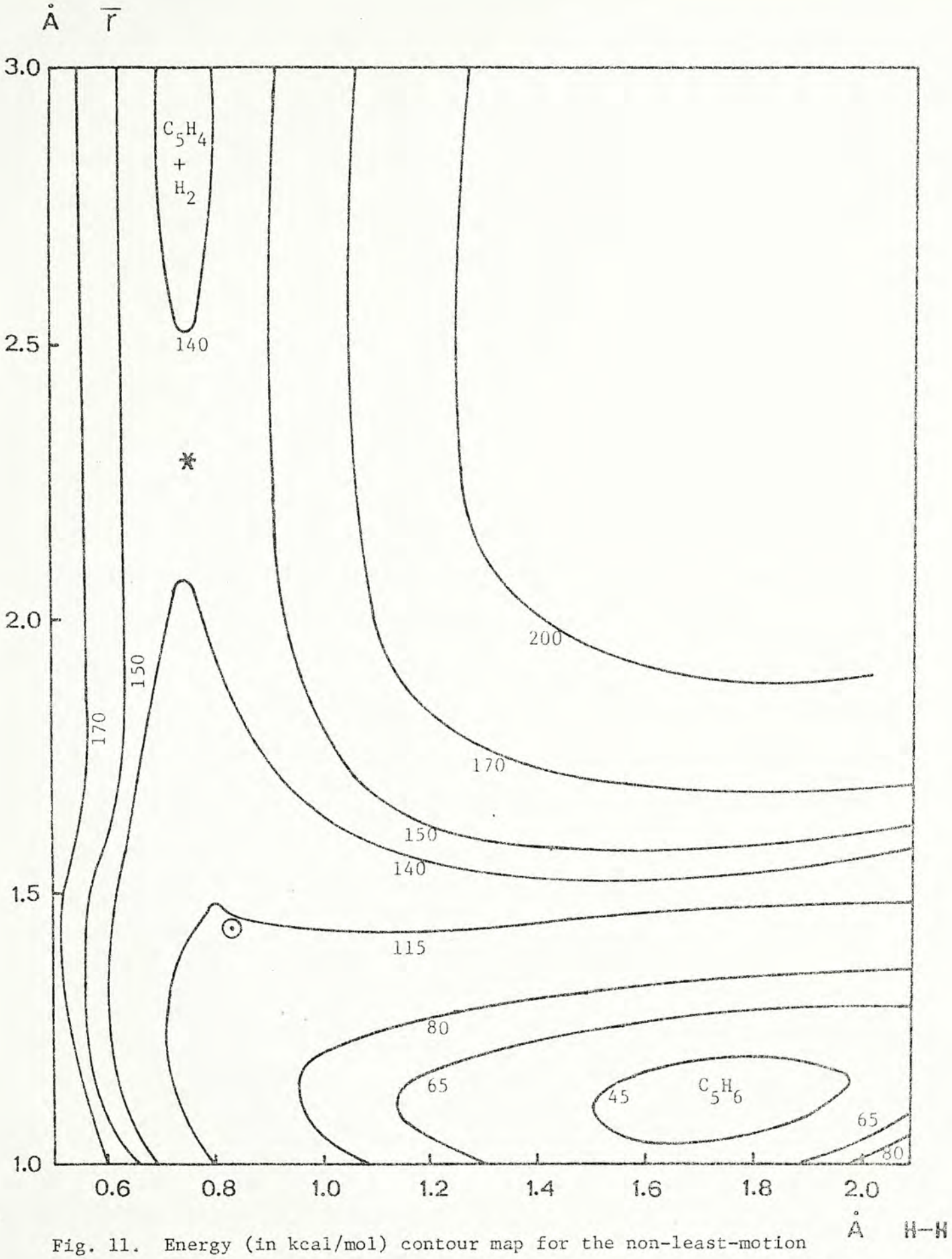


Fig. 11. Energy (in kcal/mol) contour map for the non-least-motion reaction of cyclopentadienylidene + H_2. The asterisk and ⊙ denote the saddle point and the turning point, respectively.

energy of about 2 kcal/mol for the reaction. The geometry of the transition state is shown in Fig. 12. Throughout this range, there is a steady increase in the charge of the hydrogens: from ∿0 to 0.20. However, the change in the charge of the carbenic centre is far from smooth, as shown in Fig. 13. Specifically, starting from $\bar{r} \sim 2.5$, the charge of C_1 decreases from 0.019 to -0.045 when $\bar{r}$ reaches 1.62 Å. This decrease is due both to the electron flow from H_2 and C_2 and C_3 of the diene. At $\bar{r}$ = 1.62 Å, a three-centre bond between C_1 and H_2 is formed, with E_r for C-H being -53 kcal/mol. As soon as $\bar{r}$ becomes smaller than 1.62 Å, there is a sudden increase in the C_1 charge to 0.126 (Fig. 13), mainly due to the electron withdrawl from C_1 to the diene. This increase in the C_1 charge favors further electron flow from H_2 to C_1, strengthening the three-centre bond (E_r of C-H decreases quickly to -65 kcal/mol at $\bar{r}$ = 1.60 Å) and lowering the energy of the system dramatically (by 12 kcal/mol) in the process. As shown in Fig. 14, at this point ($\bar{r} \sim 1.60$ Å), the C-C bond lengths of the five-membered ring become mearly equal (1.39-1.42 Å) and the inserting angle suddenly becomes $\sim 90^{\circ}$ (it is $\sim 27^{\circ}$ at $\bar{r}$ = 1.62 Å), very near the value for the product. From this point on, the H-H distance replaces $\bar{r}$ as the reaction coordinate. As $\bar{r}$ further decreases, the C_1 charge again starts to decrease until the truning point ($\bar{r}$ = 1.44 Å) is reached. Also, during this range, there is a redistribution of charge in the five-membered ring, making the diene system become distinguishable again. This concludes the electrophilic phase of the reaction.

When $\bar{r}$ becomes smaller than 1.44 Å, the nucleophilic phase begins. During this phase the lone pair of C_1 interacts with the σ^* orbital of H_2, making the H-H bond (H-H changes from 0.96 to 1.75 Å) and decreasing

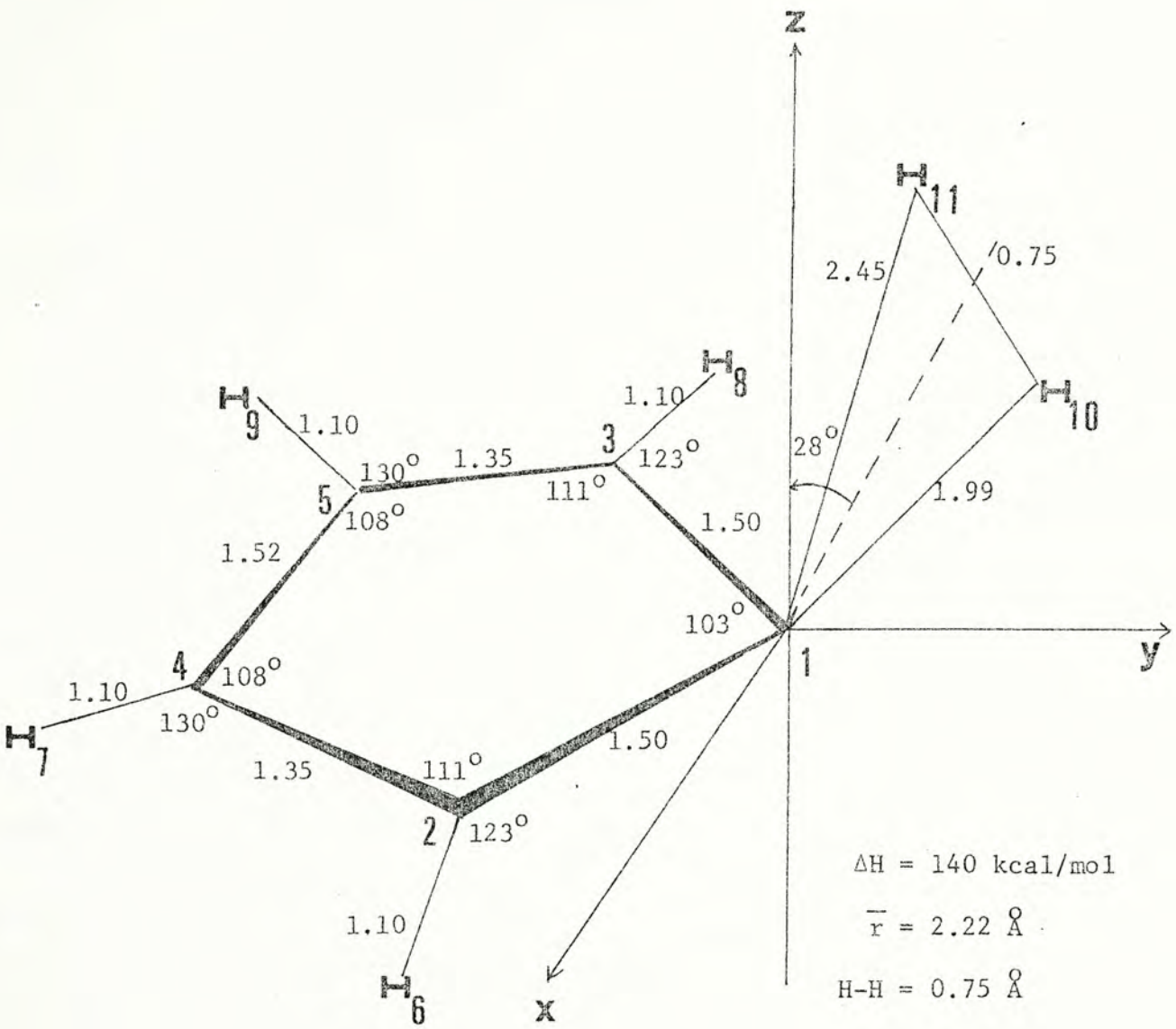


Fig. 12 Geometry of the transition state for the non-least-motion reaction of cyclopentadienylidene + H_2. Distances are in Å.

Fig. 13. Electron charge fluctuation for the non-least-motion reaction of cyclopentadienylidene + H_2

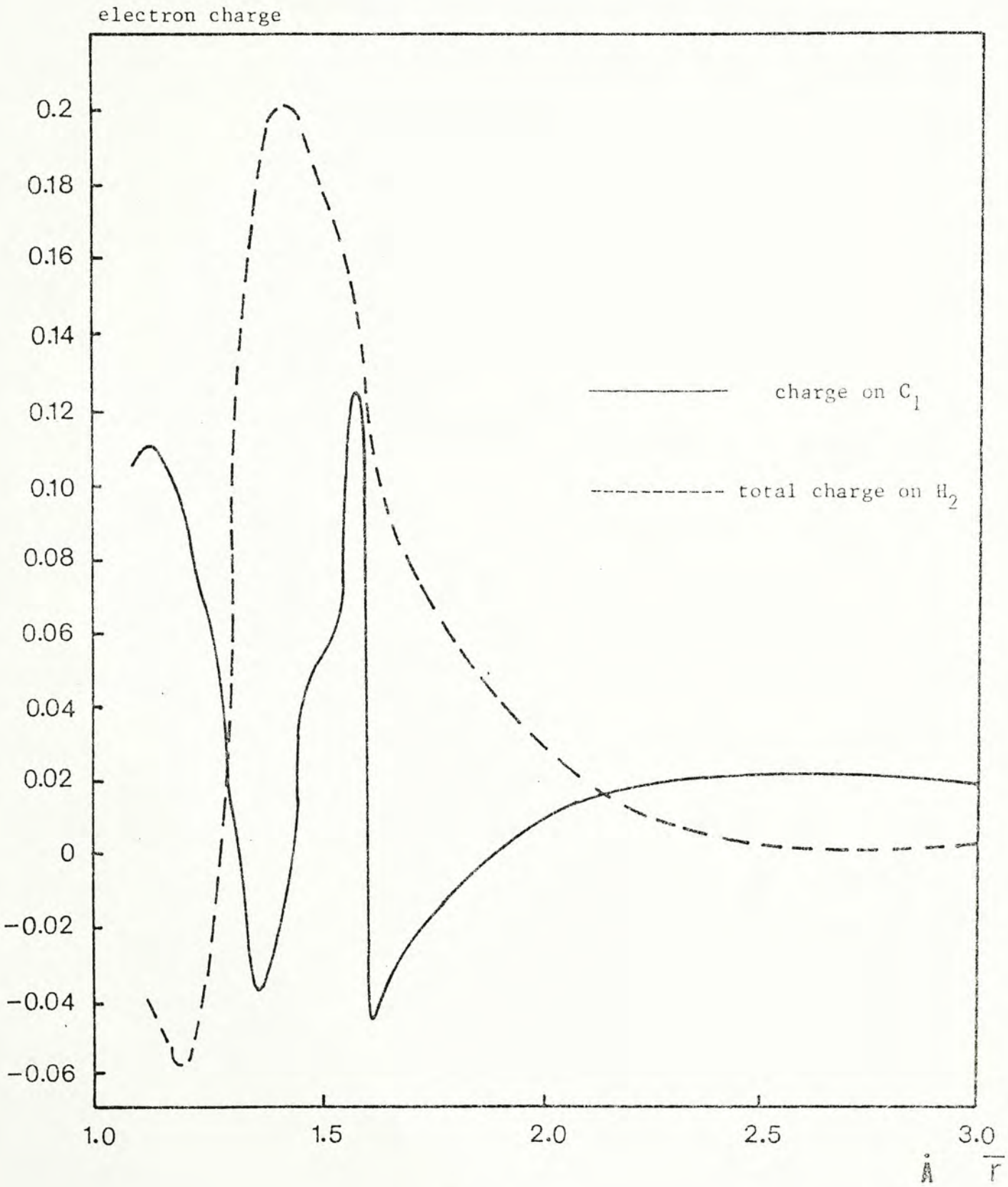
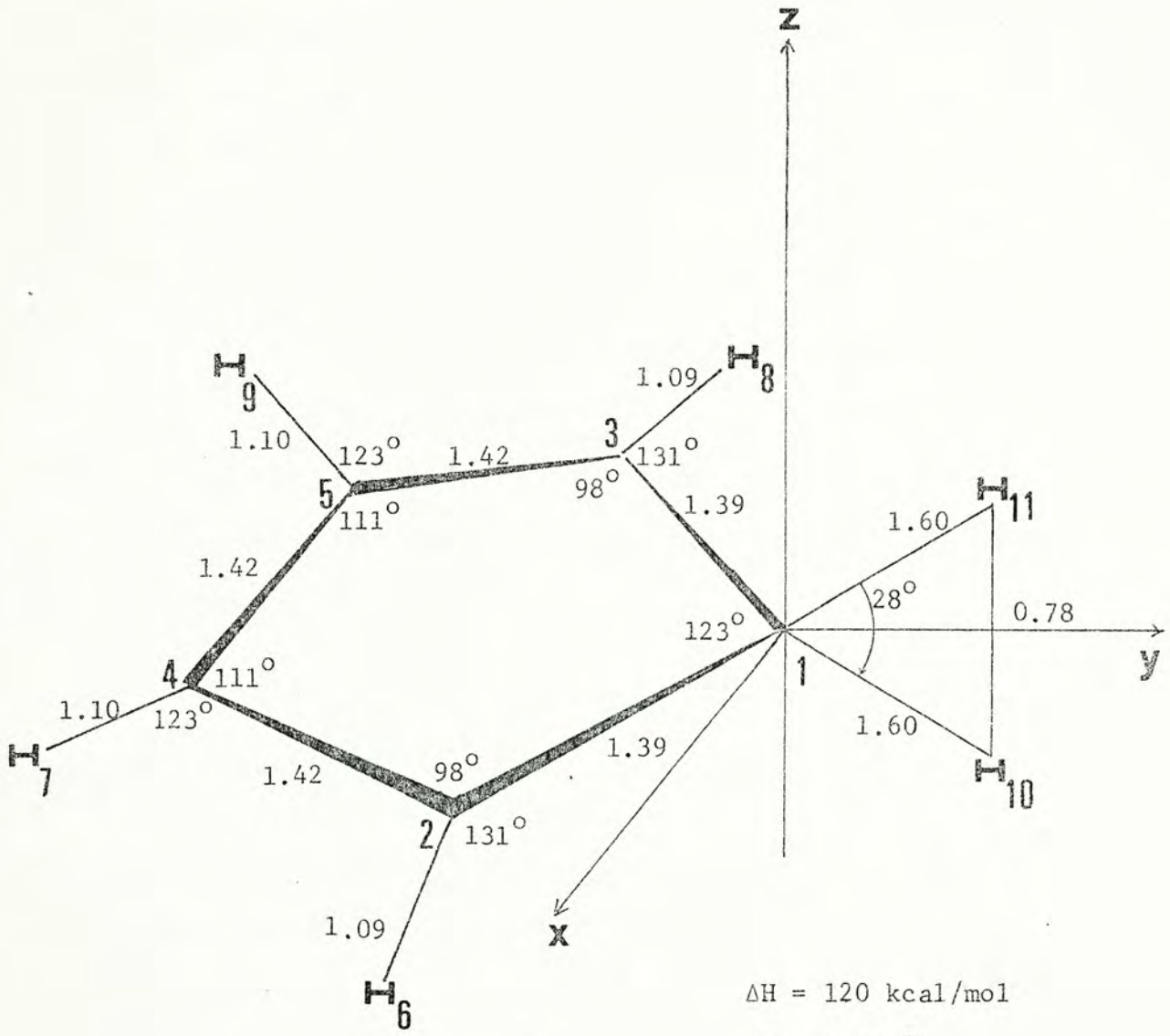


Fig. 14 Geometry of the system after a rapid electron redistribution for the non-least-motion reaction of cyclopentadienylidene + H_2. Distances are in Å.



ΔH = 120 kcal/mol

$\bar{r}$ = 1.60 Å

H-H = 0.78 Å

the charge of H_2. As far as the carbene is concerned, electron flows towards C_2 and C_3 from the other carbons, further defining the double bonds. The energy of the system decreases rapidly to that of the product.

The energy contour map for (III) + H_2 reaction is very similar to that of (II) + H_2 shown in Fig. 7. They both have low activation energies and similar positions for the transition states and turning points. Early transition states for both reactions indicate that emptiness of their p_π orbital at C_1 and the electrophilicity of the carbenic centres.

Most importantly, the conjugated diene π system in (III) serves as a reservoir for electron during the H_2 insertion. It leads to a complicated pattern of variation for the C_1 charge which is remarkably different from the other two reactions. The fluctuation of the C_1 charge promotes the vacancy for the formation of strong C-H_2 three-centre bonds. Besides, this fluctuation marks a sudden change of reaction coordinate, energy, electronic and geometrical structures.

2.4 Conclusion

In general, similar qualitative conclusions can be drawn for the insertions studied: (i) The insertion of the carbenes into H_2 is a concerted non-least-motion process with two distinguishable steps, an electrophilic phase followed by a nucleophilic phase. (ii) The electrophilic phase is characterized by the approaching H_2 to the carbene, forming a three-centre bond with the "empyt" p_π orbital of the carbenic centre and increasing its population. (iii) In the nucleophilic phase, at fairly small C-H distances, the H_a-H_b bond is broken and the H_a-C-H_b plane

rotates to its final product arrangement. [However, for the insertion of (III), the rotation of H_a-C-H_b plane occurs much earlier than turning point.] Also, back charge donation from the lone pair of the carbene to the σ^* orbital of H_2 occurs, accompanied by a rapid fall of the energy of the system.

MINDO/3 potential energy surfaces for (II) + H_2 and (III) + H_2 are very similar. They indicate that (II) and (III) have same degree of electrophilicity toward H_2. But the carbenic centre of (I) is stabilized by the presence of the aromatic ring and the empty p_π orbital is partially populated. So its electrophilicity is much reduced and this leads to the high energy barrier and delays the formation of the transition state. The insertion motion of (III) can proceed easily because the diene π system can accommodate much electron density from the carbenic centre to minimize the energy barrier during formation of the three-centre bond. The H_2 insertion of (II) is remarkably similar to that of methylene, even with the presence of a small ring.

Stereospecificity is essential for all these reactions. For all three, in order to initiate the insertions, the H_2 molecule has to rise above the molecular plane to attack the p_π orbital. It remains in this geometry until the rate-determining step is over.

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PART 3

THE LEAST-MOTION INSERTIONS OF CYCLIC CARBENES

3.1 Introduction

The least-motion insertion reactions (I) + H_2 → cyclopropene, (II) + H_2 → cyclopropane and (III) + H_2 → cyclopentadiene are "forbidden linear" cheletropic additions in Woodward-Hoffmann terms[1]. One then expects a large barrier height for these processes. The "forbiddeness" for the least-motion insertion is due to the fact that HOMO-LUMO crossing is involved. In this work, the least motion insertion reactions of (I) + H_2, (II) + H_2 and (III) + H_2 are studied by means of the MINDO/3 model.

3.2 Method of Calculations

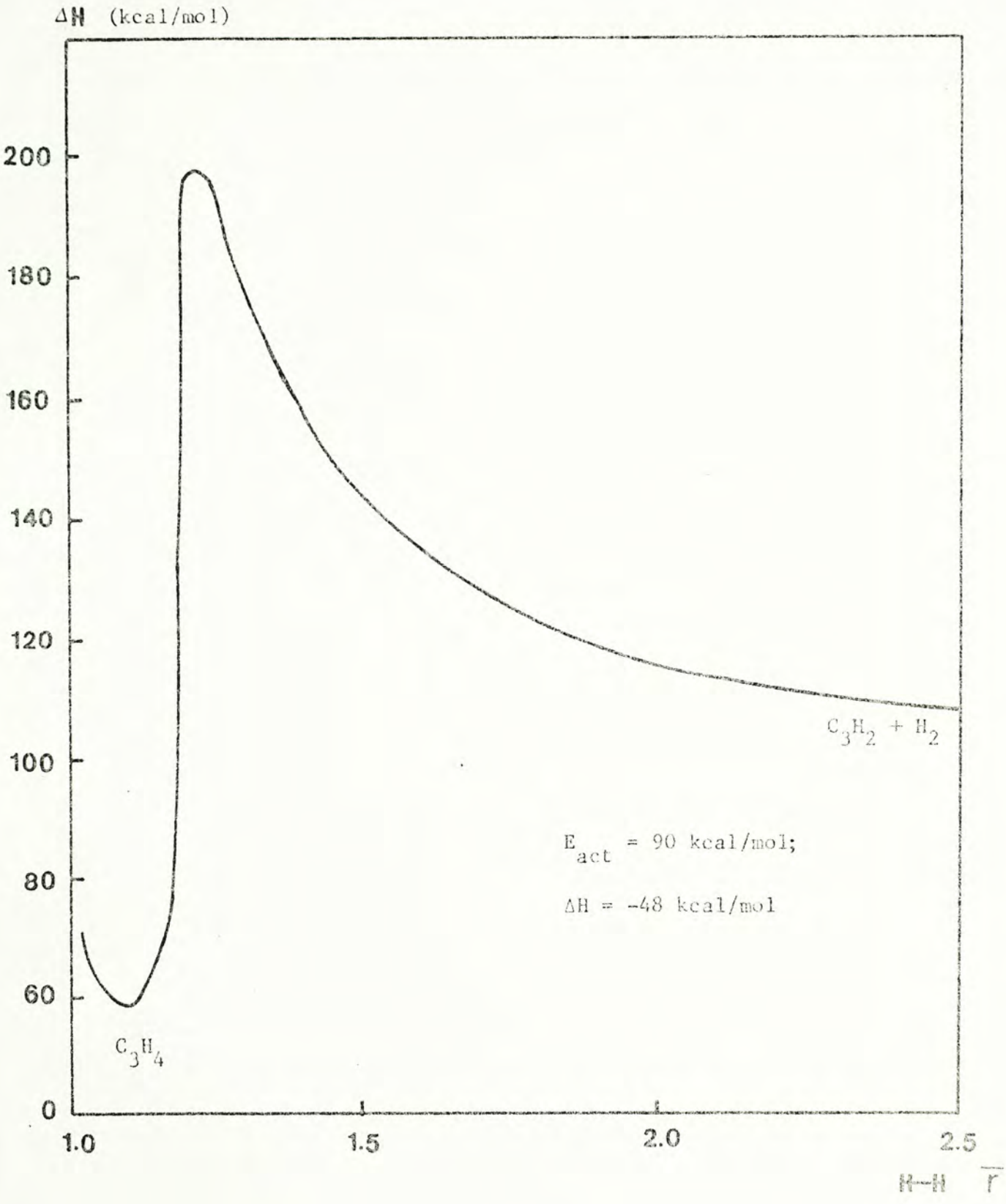
For these processes, C_{2v} symmetry is retained throughout. Energy contour maps were constructed as follows: for different given H-H, $\bar{r}$ was varied over a wide range (0.1 - 4.0 Å) and the two H atoms were lying on a symmetry plane which passed through the carbenic carbon and the midpoint of the C-C bond opposite to it. All other structural parameters were optimized.

3.3. Results and Discussions

3.3.1 The Insertion of Cyclopropenylidene into Molecular Hydrogen

The one-dimensional energy profile and two-dimensional contour map for the least-motion insertion of (I) into H_2 are shown in Figs. 1 and 2, respectively. As seen in Fig. 2, the saddle point is located at $\bar{r}$ = 1.22 Å and H-H = 0.94 Å. The activation energy is 90 kcal/mol, which is about five times that of the corresponding non-least-motion reaction. Right

Fig. 1. One-dimensional energy profile for the least-motion reaction of cyclopropenylidene + H_2.



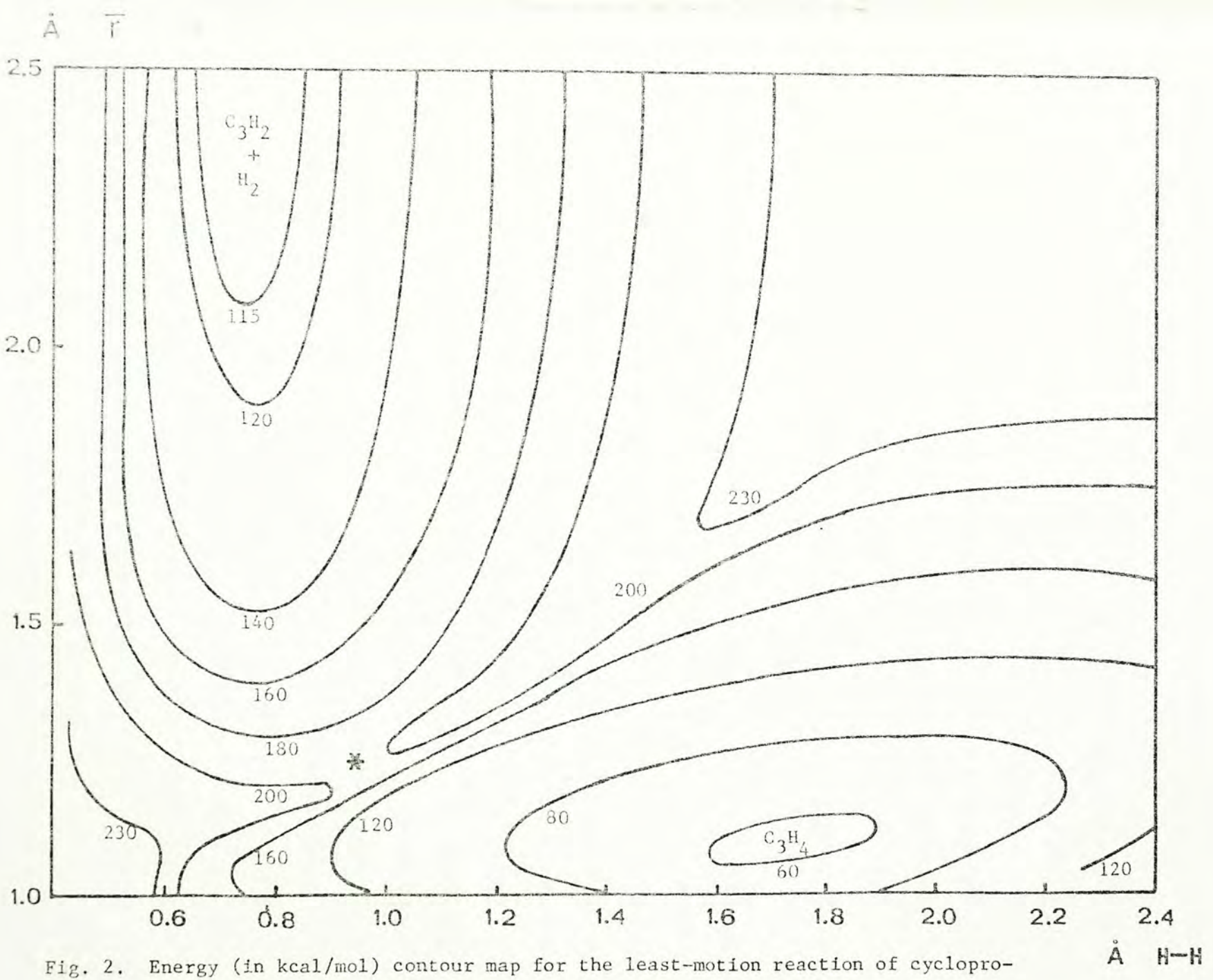


Fig. 2. Energy (in kcal/mol) contour map for the least-motion reaction of cyclopropenylidene + H_2. The asterisk denotes the saddle point.

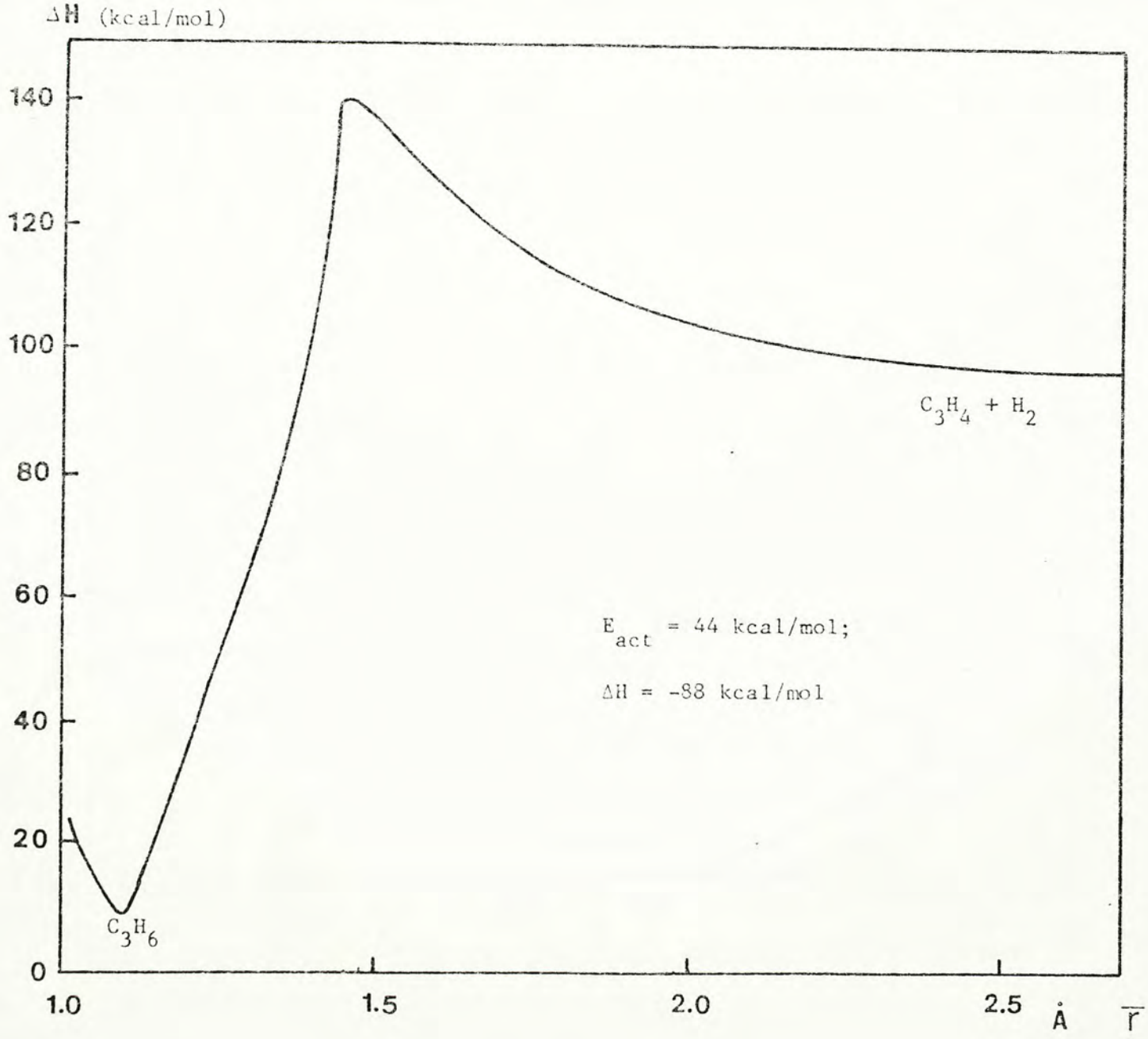
after the saddle point, for the E_r of both the C-H bonds and H-H bond, there there is a discontinuity. At the saddle point, E_r for C-H and H-H bonds are -33 and -165 kcal/mol, respectively, showing that the H-H molecule is essentially intact. Right after the saddle point, E_r for C-H and H-H bonds change abruptly to -213 and 9 kcal/mol, respectively, indicating that the C-H bonds have been formed and the H-H bond broken. Studying the electronic distributions throughout the reaction, the locations of the turning point and the saddle point are essentially the same. As in the case of non-least-motion reaction, energy drops off quickly (by 130 kcal/mol for a charge of 0.5 Å for $\bar{r}$) as soon as the nucleophilic phase begins.

Referring to the electronic structure before the turning point, C_1 acquires electron from H_2, distributing some of it to the other atoms in the carbene moiety while making a small increase in electron density in C_1. After the turning point, the charge on C_1 increases abruptly to 0.13 (-0.11 at transition state), strengthening the C_2-C_3 double bond (the E_r value decreases by 55 kcal/mol) and increasing the C_2 and C_3 populations.

3.3.2 The Insertion of Cyclopropylidene into Molecular Hydrogen

The one-dimensional energy profile and two-dimensional contour map for the titled reaction are shown in Figs. 3 and 4, respectively. Again the first phase of reaction is electrophilic because the hydrogen molecule gives up electrons from the σ orbital to C_1. However, it is an electron donating phase for the carbenic centre since only 0.032 electron is transfered from H_2 but simultaneously 0.045 electron is drawn from it to the other carbons. Unlike the (I) + H_2 system, the saddle point and the turning point do not coincide. The saddle point is located at $\bar{r}$ = 1.45 Å

Fig. 3. One dimensional energy profile for the least-motion reaction of cyclopropylidene + H_2.



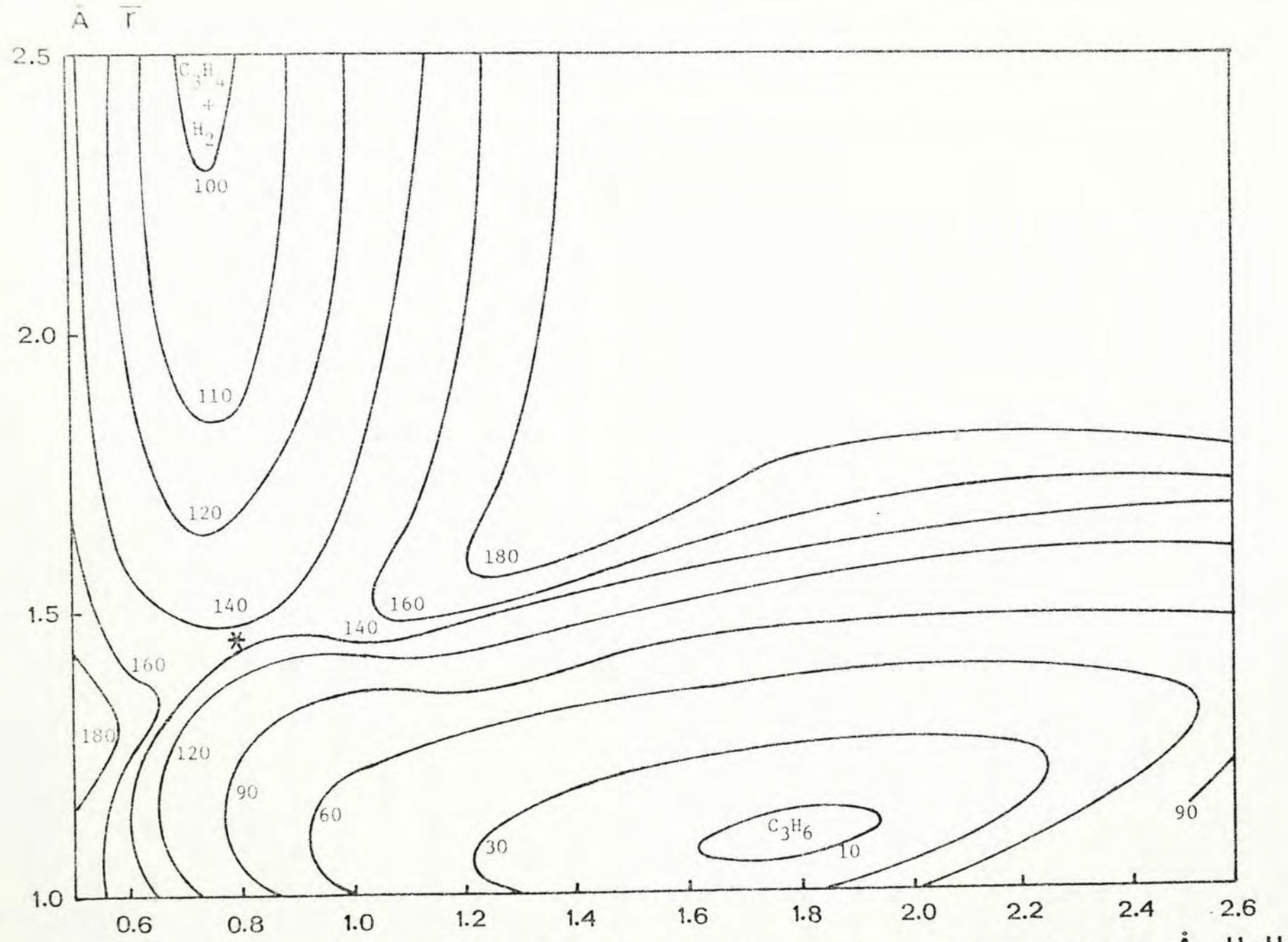


Fig. 4. Energy (in kcal/mol) contour map for the least-motion reaction of cyclopropylidene + H_2. The asterisk denotes the saddle point.

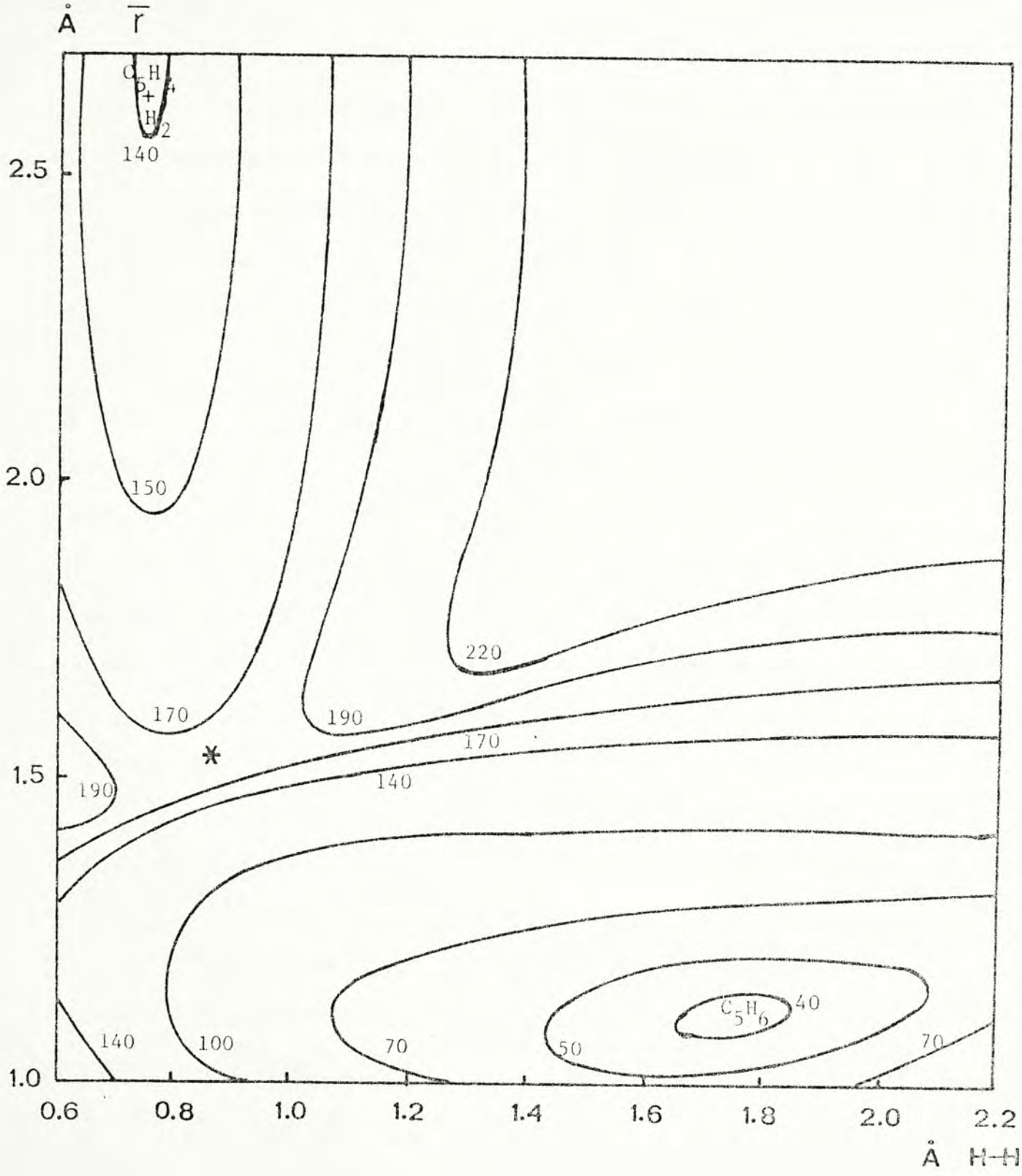
and H-H = 0.77 Å; the turning point is at $\bar{r}$ = 1.44 Å and H-H = 0.89 Å.

Unlike methylene,[2] which can open the bond angle to change the hybridization of lone pair, (II) is hindered by its ring, the lone pair is not free to rotate to minimize the repulsion between it and the approaching H_2 σ bond. Thus this cyclic saturated carbene has an activation energy of 44 kcal/mol, twice that of its linear analogue, methylene, when their least-motion insertions into H_2 are compared. The electronic configuration and geometry of transition state resemble more closely to the reactants than to the product. But since, orginally, there is only 0.13 electron in the p_π orbital of carbenic centre of (II), the promotion of electron from s orbital to it is easier than (I). Therefore the activation energy for (II) + H_2 is much smaller. On crossing the transition state, about 0.6 electron is removed from the highly populated s orbital (with 1.57 electron) to the p_π orbital. It facilitates the formation of C-H bonds, with their E_r being -108 kcal/mol, thus lowering the energy of the system as shown in Fig. 3. Besides, reaction coordinate changes from $\bar{r}$ to H-H separation and electronic configuration now resembles that of the product, as the hydrogens are carrying negative charge.

3.3.3 The Insertion of Cyclopentadienylidene into Molecular Hydrogen

In Fig. 5, the two-dimensional contour map for (III) + H_2 in C_{2v} symmetry is shown. The potential energy surfaces for (I), (II) or (III) to react with H_2 in the least-motion pathway are very similar. As shown in Fig. 5, the saddle point occurs in $\bar{r}$ = 1.55 Å, H-H = 0.80 Å and the energy barrier is 37 kcal/mol. Similar to the previous reactions, on crossing the transition state, there is great change in energy, electronic

Fig. 5. Energy (in kcal/mol) contour map for the least-motion reaction of cyclopentadienylidene + H_2. The asterisk denotes the saddle point.



distribution, and geometry of the system. From Fig. 6, the one-dimensional energy profile, we observe the rapid fall in energy (60 kcal/mol within 0.05 Å change of $\bar{r}$).

Before $\bar{r}$ = 1.55 Å, the carbenic centre is losing electrons to its neighbours. In spite of the flowing of electron from the H_2 σ bond, its charge becomes more positive. We can divide the reaction path into two phases in terms of the charge on H_2. In the first phase, electron flows from H_2 to the carbene. The flow is accelarated suddenly after the saddle point is reached. Within the carbene moiety, electron is first drawn from C_1 to the diene; then from the diene back to C_1. The second, nucleophilic phase begains at $\bar{r}$ = 1.46 Å. In this phase, back-donation from the lone pair to σ^* of H_2 occurs and the H-H separation widens until the product is formed.

As in the non-least-motion reaction, the diene of (III) helps to accommodate electron from the p_π orbital of the carbenic centre, which facilitates the approach of H_2 by enhancing the electron promotion from the lone pair to the empty p_π orbital. In the process, the redistribution of electrons localizes the two π bonds.

The geometry immediately after transition state is similar to that of the non-least-motion reaction. The five C-C bonds are of similar lengths, about 1.41 Å. The electrophilicity of the carbenic centre contributes much to the formation of new C-H bonds, whose E_r decreases sharply from -4.5 kcal/mol to -70 kcal/mol on crossing the saddle point. The E_r value of C-H bonds then decrease further to -188 kcal/mol after the breaking of the H-H bond.

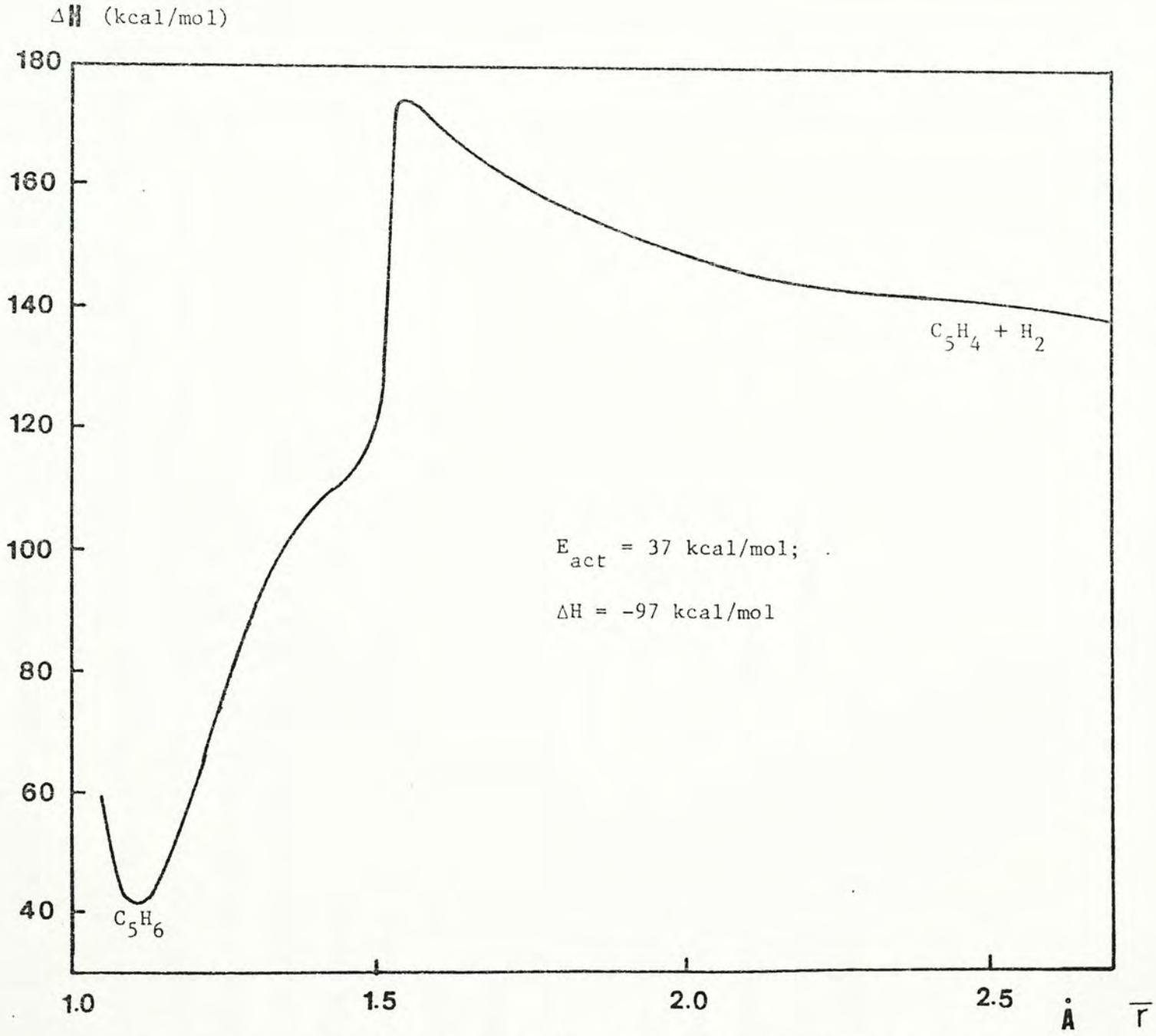


Fig. 6 . One-dimensional energy profile for the least-motion reaction of cyclopentadienylidene + H_2.

3.4 Conclusion

Orbital crossing plays an important role in the Woodward-Hoffmann interpretation of organic reactivity. The repulsions between the lone pairs of carbenes and the σ bond of the approaching H_2 account for the large activation energies. The symmetry restrictions imposed on the least-motion reactions forbid the reactants to follow low-energy barriers. Thus stereospecificity is a dominant factor for these reactions to proceed. This part of study, together with the results of Part 2, once again illustrates Zimmerman's viewpoint[3] that reduction of symmetry will make certain reactions less forbidden. It has been considered that the perturbations associated with such a reduction of symmetry would not be sufficient to change drastically the features of the potential energy surfaces.

In the systems that have been studied in Part 2, it appears that reduction of symmetry (i.e., non-least-motion paths) allows interaction between the bonding orbital of H_2 and the 'empty' p_π orbital of the carbenic centre, leading to a removal or a drastic lowering of energy barriers; the optimium reaction path avoids maximum symmetry and is determined by the topology of the orbitals involved.

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